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Coal Gasifier Parameters Influencing Environmental Pollutant Production

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Protection Agency
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Jun 81

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EPA-600/7-81-098

RTI/1934/00-03F

June 1981

COAL GASIFIER PARAMETERS INFLUENCING ENVIRONMENTAL POLLUTANT PRODUCTION

by

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U. S. ENVIRONMENTAL PROTECTION AGENCY
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A series of fixed-bed coal gasification and pyrolysis tests have been performed in a laboratory-scale reactor of 6.6 cm inside diameter. Chemical analyses were conducted on the product gas, the aqueous condensate, the tar, and the solid residue from the tests. The effects of process variables, such as feed mode, catalytic treatment, pressure, mesh size, and coal type, upon byproduct and pollutant yields are described. The production of gaseous sulfur compounds, benzene and derivatives (BTX), phenolics (phenol, cresols, and xylenols), and tar have been measured, and the fate of trace elements such as arsenic, selenium, and lead has been determined. Byproduct production associated with the pyrolysis phase of gasification has been investigated with emphasis on the effects of particle size, residence time, and atmosphere. Experiments conducted with six U.S. coals ranging from lignite to anthracite are described. Continuous operation, ...
KEYWORDS: *Coal gasification, *Gas analysis.

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ABSTRACT

A series of fixed-bed coal gasification and pyrolysis tests have been performed in a laboratory-scale reactor of 6.6 cm inside diameter. Chemical analyses were conducted on the product gas, the aqueous condensate, the tar, and the solid residue from the tests. The effects of process variables, such as feed mode, catalytic treatment, pressure, mesh size, and coal type, upon byproduct and pollutant yields are described. The production of gaseous sulfur compounds, benzene and derivatives (BTX), phenolics (phenol, cresols, and xylenols), and tar have been measured, and the fate of trace elements such as arsenic, selenium, and lead has been determined. Byproduct production associated with the pyrolysis phase of gasification has been investigated with emphasis on the effects of particle size, residence time, and atmosphere.

Experiments conducted with six U.S. coals ranging from lignite to anthracite are described. Continuous operation was found to result in greatly reduced tar and phenolic production. When the entire mass of coal was introduced at the beginning of the test, effluent stream compositions more closely approached those of larger scale, fixed-bed gasifiers. Initial work on this project was reported in EPA-600/7-78-171; three more recent reports were EPA-600/7-79-200 through EPA-600/7-79-202.

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CONTENTS

ABSTRACT ii
FIGURES iv
TABLES v
1.0 INTRODUCTION 1
2.0 CONCLUSIONS 5
3.0 EFFECTS OF CONTINUOUS COAL FEED 7
4.0 EFFECT OF ADDITION OF ALKALI METALS 19
5.0 EFFECTS OF PRESSURE AND MESH SIZE 30
6.0 EFFECTS OF COAL TYPE ON YIELDS OF POLLUTANTS AND BYPRODUCTS . . 43
7.0 TRACE ELEMENT DISPOSITION IN THE RTI GASIFIER: RELATIONSHIP TO PROCESS CONDITIONS 55
8.0 POLLUTION EVOLUTION IN PYROLYSIS TESTS 73

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EPA-287 (Cite)
(4-76)

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TOP OF IMAGE AREA
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FIGURES

Number		Page
1-1	Gasification and sampling systems.	2
3-1	Semicontinuous gasification sequence	9
3-2	Continuous gasification sequence	10
6-1	Effect of rank on byproduct production from airblown, fixed bed, semicontinuous gasification of 8x16 mesh coal at 200 psi.	43
7-1	Correlation of arsenic volatilization with A. carbon conversion and B. sulfur conversion. Gasification tests with Illinois No.6 coal	59
7-2	Correlation of selenium volatilization with carbon conversion during gasification of Illinois No.6 coal.	62
7-3	Correlation of selenium volatilization with carbon conversion during gasification of western subbituminous coals	62
7-4	Correlation of lead volatilization with sulfate sulfur in the residue for gasification tests with subbituminous coals. . . .	67
8-1	Gasifier results; run 36, North Dakota lignite	74
8-2	Operating conditions for pyrolysis test P-1: Base case. . . .	78
8-3	Evolution profiles for major gases from pyrolysis test P-1: Base case.	79
8-4	Evolution rates during pyrolysis as predicted by model of RTI reactor.	82
8-5	Evolution rates for pyrolysis test P-2: Large particles . . .	83

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BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-267 (Circ.) (4-78)

TABLES

Number		Page
3-1	COMPARISON OF OPERATING CONDITIONS, PRODUCT AND BYPRODUCT OUTPUTS	11
3-2	COMPARISON OF OPERATING CONDITIONS, PRODUCT AND BYPRODUCT OUTPUTS	12
3-3	COMPARISON OF OPERATING CONDITIONS, PRODUCT AND BYPRODUCT OUTPUTS	13
3-4	TAR AND BTX YIELDS FOR CONTINUOUS AND SEMICONTINUOUS OPERATING MODES (mg/g coal)	17
4-1	RAW FEED ANALYSES - AS GASIFIED	21
4-2	RESIDUE ANALYSES.	22
4-3	GASIFIER OPERATING CONDITIONS	23
4-4	PRODUCT GAS COMPOSITIONS (MOISTURE-FREE BASIS).	25
4-5	TAR YIELD AND COMPOSITION	27
5-1	RAW COAL ANALYSES FOR PRESSURE AND MESH SIZE EXPERIMENTS.	31
5-2	RESIDUE ANALYSES: PRESSURE AND MESH SIZE EXPERIMENTS	32
5-3	GASIFIER OPERATING CONDITIONS - ILLINOIS NO.6 COAL.	33
5-4	GASIFIER OPERATING CONDITIONS - NORTH DAKOTA BEULAH/ZAP LIGNITE	34
5-5	PRODUCT GAS COMPOSITION (MOISTURE-FREE BASIS) - ILLINOIS NO.6 COAL	36
5-6	PRODUCT GAS COMPOSITIONS (MOISTURE-FREE BASIS) - NORTH DAKOTA BEULAH/ZAP LIGNITE	37
5-7	TAR YIELD AND COMPOSITION - ILLINOIS NO.6 COAL.	39
5-8	TAR YIELD AND COMPOSITION - NORTH DAKOTA BEULAH/ZAP LIGNITE	40
6-1	OPERATING DATA--AIRBLOWN, FIXED BED, SEMICONTINUOUS GASIFICATION OF 8x16 MESH COAL AT 200 PSI	44
6-2	COMPOSITION OF BYPRODUCT TAR FROM AIRBLOWN, FIXED BED, SEMICONTINUOUS GASIFICATION OF 8x16 MESH COAL AT 200 PSIG	47
6-3	SULFUR CONVERSION AND RETENTION IN AIRBLOWN, FIXED BED, SEMICONTINUOUS GASIFICATION OF 8x16 MESH COAL AT 200 PSI (µg/g sulfur input)	49

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PAGE NUMBER
EPA-287 (Rev-1 (4-76)

Tables, con't

Number		Page
6-4	NITROGEN CONVERSION AND RETENTION IN AIRBLOWN, FIXED BED, SEMICONTINUOUS GASIFICATION OF 8x16 MESH COAL AT 200 PSI (µg/g nitrogen input)	51
8-1	CHARACTERISTICS OF WYOMING SUBBITUMINOUS COAL USED IN PYROLYSIS RUNS.	76
8-2	SUMMARY OF PYROLYSIS TESTS CONDITIONS	77

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1.0 INTRODUCTION

Technology for the conversion of coal to gaseous fuel has been available for many years. Renewed interest in coal gasification processes, motivated by greatly increased petroleum prices and anticipated shortages of oil and natural gas, has stimulated considerable research into process improvements. Gaseous fuels are inherently easier to transport and distribute than coal. With increasing constraints on the discharge of oxides of sulfur and nitrogen, gaseous fuels may require less expensive pollution control systems than coal and oil. Additionally, indirect liquefaction of coal via catalytic reaction of coal-derived gas to produce oil substitutes is approaching economic feasibility in the United States.

The increasing likelihood of large-scale commercial development of coal gasification in the United States has generated concern over the pollutants produced in these processes. The Research Triangle Institute has performed a five-year study directed towards quantifying the production of byproducts and pollutants from coal gasification processes and investigating the influence of processing conditions on these materials. The project was sponsored by the Industrial Environmental Research Laboratory of the U.S. Environmental Protection Agency at Research Triangle Park, North Carolina.

The experiments were conducted in a laboratory-scale coal gasification system designed and constructed at RTI. A simplified schematic of the system is shown in Figure 1-1. The reactor is a 100-cm length of nominal three-inch Schedule 160, type 310 stainless steel pipe, fitted with ring joint flanges at both ends.

A flow distributor constructed of a porous ceramic disk mounted on a stainless steel plenum chamber is inserted into the reactor to a height of approximately 30 cm from the bottom reactor flange. The flow distributor serves as a support for the coal bed. The reactor is enclosed in a vertical tube furnace with three independently controlled heating zones. Superheated steam is generated by pumping deionized water with a positive displacement,

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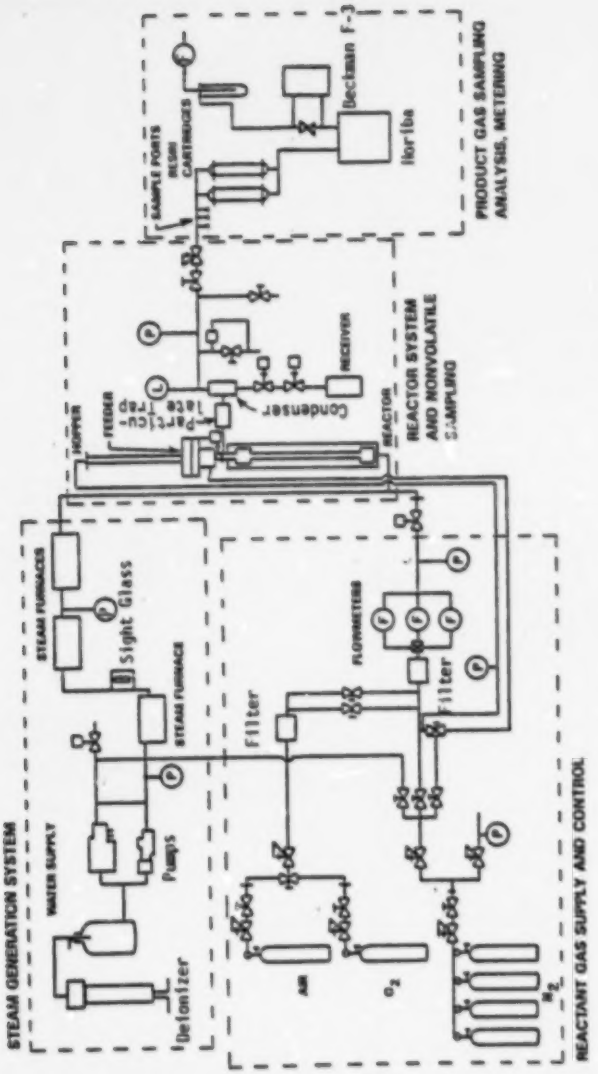

Figure 1-1. Gasification and sampling systems.

packed, plunger-type metering pump through stainless steel tubing enclosed in a series of three electrically heated furnaces. Nitrogen, oxygen, or air from standard compressed gas cylinders are mixed with the superheated steam and enter the reactor through a tube connecting the bottom flange and the flow distributor.

Coal was added to the reactor from the top. Usually coal from a pressurized feed hopper was added batchwise through a pneumatically operated ball valve. In some cases a rotating-disk coal feeder was used to continuously supply coal to the reactor. Gases flowed out of the top of the reactor through a tube in the upper flange into a water-jacketed condensate trap. A two-phase mixture collected in this trap: a tar phase and an aqueous condensate phase made up of moisture from the coal and unconverted reactant steam. The condensate trap was periodically emptied through a pressure lock arrangement using two remotely operated ball valves. The gas flowed from the condensate trap through an adjustable back pressure regulator where the pressure was reduced to slightly above atmospheric. The gas then entered a sampling manifold with provisions for discrete sampling in glass bulbs, resin adsorption, and an impinger. Finally, the gas passed through a dry test meter and was vented.

The reactor temperature was determined using a multipoint thermowell containing up to 12 chromel-alumel thermocouples. This thermowell was inserted through the upper flange of the reactor to a point slightly above the flow distributor. The thermocouples initially were connected to digital displays. For the more recent tests, the thermocouples were also connected to analog-to-digital converters and automatically stored on magnetic disks. Additional thermocouples were used to measure the temperature of the inlet steam and condensate trap. The pressure at the steam-air inlet and at the exit of the condensate trap was measured both by transducers and by bourdon tube gauges. The transducer outputs were displayed digitally and stored.

A variety of fuels have been gasified in the laboratory system. This report deals with experiments made with the following fuels:

1. North Dakota Beulah/Zap lignite
2. Montana Rosebud/McKay subbituminous coal
3. Wyoming Smith/Roland subbituminous coal
4. Illinois No.6 bituminous coal
5. West Kentucky No.9 bituminous coal
6. Pennsylvania Bottom Red Ash anthracite coal

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Additional reports have been prepared which describe the environmental hazards[1] of, and possible control technologies[2] for, the pollutants generated in the laboratory gasification system.

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1. Gangwal, S. K., J. G. Cleland, and R. S. Truesdale. Evaluation of Relative Environmental Hazards from a Coal Gasifier. RTI/1934/00-02F, April 1981.

2. McMichael, W. J., S. K. Gangwal, and D. A. Green. Vapor Phase Cracking and Wet Oxidation as Potential Pollutant Control Techniques for Coal Gasification. RTI/1934/00-01F, April 1981.

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2.0 CONCLUSIONS

Operation of the laboratory gasifier in the continuous mode resulted in a higher ratio of carbon dioxide to carbon monoxide, and a greater yield of benzene, toluene, and xylenes (BTX) than operation in the semicontinuous mode. The continuous gasification mode also generated less tar and less phenolic material than the semicontinuous mode, and the tar that was produced in continuous testing was lower in tar acids than that produced in semicontinuous testing. The tar produced in semicontinuous testing was quite similar to that produced in larger scale, intermittently fed, fixed-bed gasifiers in both composition and yield.

Gasification of Illinois No.6 coal that had been treated with alkali metal compounds indicated that the catalytic treatment did not increase reaction rates, lower the reaction temperatures, or decrease caking and swelling tendencies in the laboratory reactor. Treatment with K_2CO_3 reduced hydrogen sulfide production and increased sulfur and mercury retention in the solid residue but had no effect on nitrogen retention. Treatment with NaOH at a much lower level reduced tar production but did not change the elemental composition of the tar; treatment with NaOH did not affect nitrogen or sulfur retention but did increase the retention of mercury in the solid residue.

When the particle size of the coal fed to the gasifier was doubled, the product gas was higher in carbon monoxide relative to carbon dioxide. For Illinois No.6 coal, larger particles produced less BTX and a tar that was higher in acids. Doubling the particle size of North Dakota lignite resulted in an increased tar yield.

Lower pressure gasification produced more carbon monoxide relative to carbon dioxide and tar with a decreased polynuclear aromatic content. With Illinois No.6 coal, lower pressure operation resulted in a product gas higher in carbon monoxide relative to hydrogen and a greatly increased tar yield.

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Both tar yield and BTX yield increased with rank from lignite to bituminous. Anthracite coal produced no tar and very little BTX. Phenol, cresols, and xylenols (PCX) production generally decreased with increasing coal rank. Lignite and subbituminous coal produced tar with a higher proportion of acids and a lower proportion of bases than the tar from bituminous coals. Consistent with behavior in combustion processes, more sulfur was retained in the solid residue from lignite and subbituminous coals than in the solid residue from bituminous coal. Nitrogen retention in gasification residue did not vary consistently with rank.

In tests with Illinois No.6 coal, arsenic volatilization was strongly correlated with carbon and sulfur conversion. Selenium volatilization was significantly correlated with carbon conversion but not with sulfur conversion. Mercury was completely volatilized in all tests for which data is available except for tests where the feed coal was treated with alkali metal compounds; treatment with NaOH did, however, increase the volatility of beryllium.

From pyrolysis experiments conducted in an inert atmosphere, it was concluded that particle size had no effect on BTX production or rate of devolatilization but did influence drying time. When Wyoming subbituminous coal was heated in a hydrogen-carbon monoxide atmosphere, initial hydrogen sulfide production equaled that of pyrolysis in a nitrogen atmosphere. Additional hydrogen sulfide was produced after pyrolysis was complete when the surrounding atmosphere contained hydrogen. At no stage of the pyrolysis experiment was hydrogen sulfide in equilibrium with carbonyl sulfide; it was concluded that hydrogen sulfide evolved from the coal and its hydrolysis was kinetically limited.

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3.0 EFFECTS OF CONTINUOUS COAL FEED

The experimental gasification program began with an investigation of pollutant production in the fixed-bed semicontinuous mode. In more than fifty experiments which were conducted, coal was added to a preheated reactor over the course of a few minutes, after which steam and air were continuously introduced from the bottom of the coal bed for one to six hours until the carbon in the initial coal charge was substantially depleted. Details of operation, sampling, and chemical analyses are given in previously issued reports.[1,2,3,4]

The reaction environment provided in this mode of experiment differed in several ways from the environment provided in larger scale gasification systems. The major difference between the semicontinuous mode of the experimental gasifier and that of larger scale fixed- or gravitating-bed gasifiers was the temperature at which devolatilization took place. The introduction of a large batch of cold coal to the reactor depressed the temperature and a longer, slower particle heating rate resulted. In a continuous gasification system, small increments of cold coal are added to the reactor and the overall temperature profile of the gasifier does not vary with time.

A second difference between continuous and semibatch operation is the gaseous environment present as the coal is fed to the reactor and heated. In a continuous feed, fixed-bed gasifier, the coal is typically fed from the top of the gasifier and falls freely to a coal bed supported by a grate. The falling coal is exposed to a countercurrent flow of gasification products and unconverted reactant steam. In the semicontinuous mode, the coal is pyrolyzed in the presence of pyrolysis products rather than gasification products; in addition, during the early stages of pyrolysis unconverted oxygen may be present and may take part in secondary reactions with pyrolysis products.

A final difference between continuous and semibatch gasification is the depth of the coal bed in the reactor. In the semibatch laboratory gasifier,

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bed depths immediately after the coal was introduced were extremely high (bed height/diameter ≈ 10). As the tests proceeded, the bed depth decreased with the zone of reaction moving from the bottom up. A relatively inert ash layer built up from the bottom of the reactor and the entire bed contracted as the carbon was converted. The entire coal charge was pyrolyzed, however, in the presence of a deep bed, and pyrolysis products from the lower portions of the coal bed were contacted with coal and char in the upper portions of the coal bed as they traveled towards the reactor exit. In a continuous gasification process, these pyrolysis products would evolve from the coal particles either during the free fall to the coal bed or soon afterward. Thus secondary reactions thought to take place on the surface of other coal or char particles would be reduced.

In order to measure pollutant production in a system more closely related to the environment in a larger scale coal gasifier, the laboratory gasifier was modified to permit continuous addition of coal. A rotating disk coal feeder, modeled after the feeder used in the SYNTHANE process development unit at the Pittsburgh Energy Technology Center, was fabricated and mounted on the laboratory gasifier in place of the coal hopper. A schematic of the two feed modes are shown in Figures 3-1 and 3-2.

In Figure 3-1a, the empty reactor is shown with the coal loaded in the hopper. The ball valve is then opened and the coal falls to the flow distributor, the entire charge being dropped within a few minutes. Figure 3-1b shows the reactor configuration shortly after the coal has been dropped, Figure 3-1c shows the partially depleted coal bed, and Figure 3-1d shows the ash residue after substantially all of the carbon has been reacted.

Figure 3-2 illustrates the continuous feed sequence; Figure 3-2a shows the reactor with the feeder off while the system is preheated. Figures 3-2b and 3-2c show the progressive feeding of coal particles to the reactor and the buildup of char and ash on the flow distributor. Figure 3-2d shows the ash residue in the reactor after all of the coal has been fed, the feeder stopped, and the material remaining in the bed substantially depleted of carbon.

A comparison of operating conditions and product and byproduct outputs is given in Tables 3-1 through 3-3 for semicontinuous and continuous feed tests using Montana and Wyoming subbituminous coals and North Dakota lignite.

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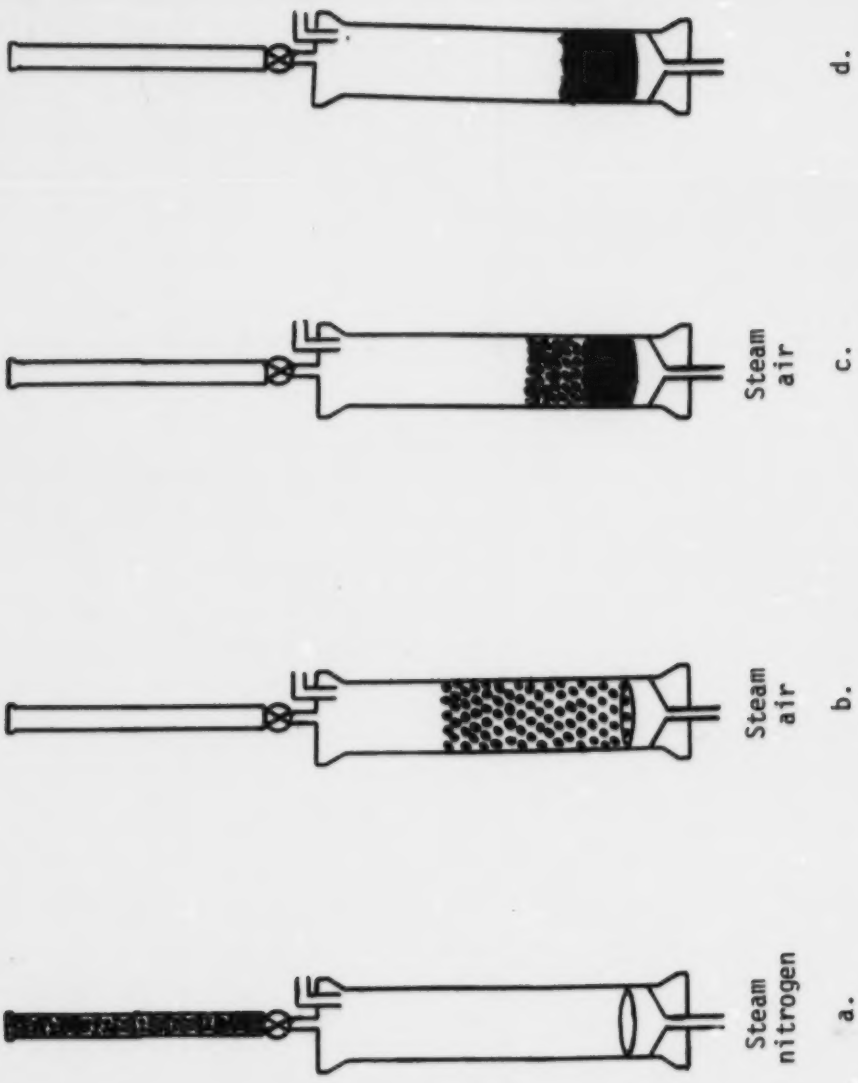

Figure 3-1. Semicontinuous gasification sequence.

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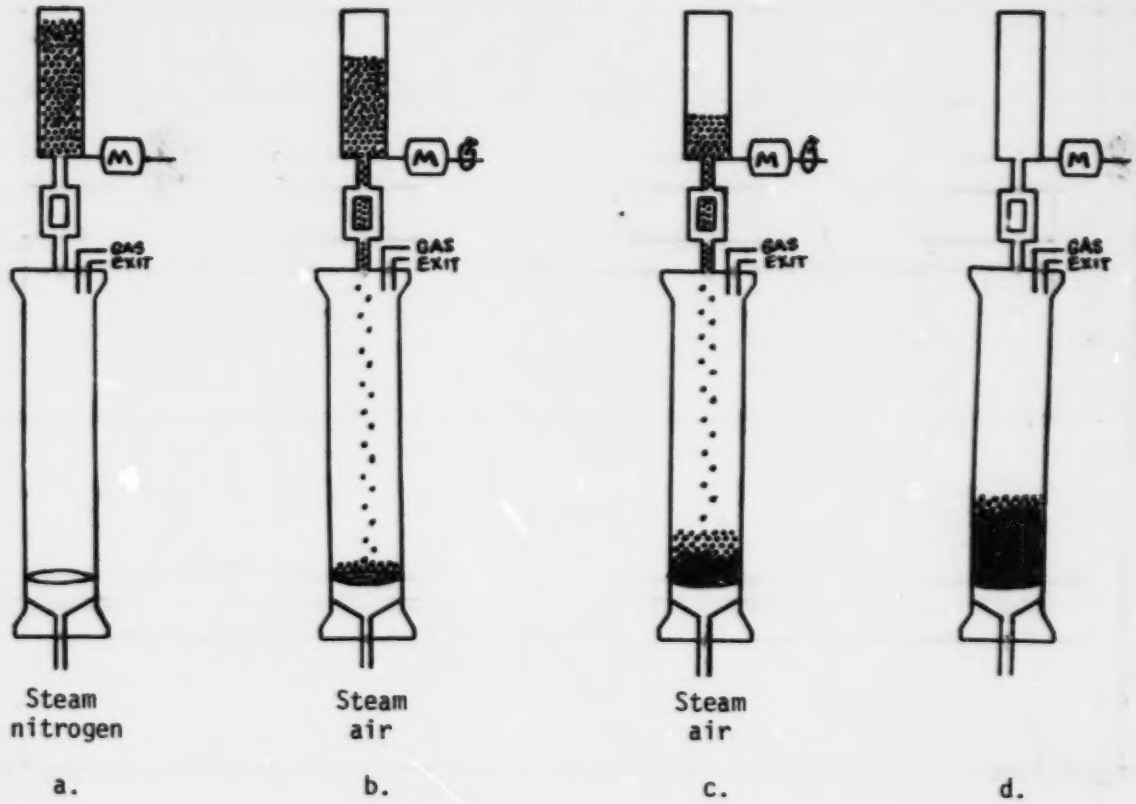

Figure 3-2. Continuous gasification sequence.

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TABLE 3-1. COMPARISON OF OPERATING CONDITIONS, PRODUCT AND BYPRODUCT OUTPUTS

	Continuous		Semicontinuous
Feed	N.D. Zap Lignite		N.D. Zap Lignite
Test	C-1		43
Mesh	8 x 16		8 x 16
Pressure	115 psia		200 psia
Air/steam g/g	3.0		4.8
Carbon conversion %	98		99
S conversion %	72		65
N conversion %	97		100
Tar yield µg/g coal	4.8		7.2
Average max. temp.°C	988	975	914
Gas comp. %	overall	steady	
CH_4	2.9	3.2	2.5
CO	18.4	21.5	21.9
CO_2	12.1	11.7	9.5
H_2	15.3	18.3	13.0
N_2	51.3	45.2	53.0
BTX (gas phase) µg/g coal	6.6E3	1.0E4	1.4E3
PCX tar µg/g coal	3		1200
PCX cond. µg/g coal	50		2000
PCX total µg/g coal	53		3200
Tar: acids %	1.2		25.3
bases %	3.2		5.4
insoluble %	11.2		5.7
NPN %	16.7		20.7
PNA %	62.2		33.2
PN %	5.5		9.7

BTX = benzene, toluene, xylene
PCX = phenol, cresols, xylenols
NPN = Nonpolar neutrals
PNA = Polynuclear aromatics
PN = Polar neutrals

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TABLE 3-2. COMPARISON OF OPERATING CONDITIONS, PRODUCT AND BYPRODUCT OUTPUTS

	Continuous		Semicontinuous
Feed	Wyoming Smith/Roland		Wyoming Smith/Roland
Test	C-2		47
Mesh	8 x 16		8 x 16
Pressure	200 psia		200 psia
Air/steam g/g	2.9		4.3
Carbon conversion %	96		98
S conversion %	96		94
N conversion %	97		94
Tar yield µg/g coal	4.4		20.8
Average max. temp.°C	985	978	946
Gas comp. %	overall	steady	
CH_4	5.2	6.4	4.6
CO	17.0	19.7	19.8
CO_2	13.3	17.0	7.4
H_2	10.9	14.9	8.8
N_2	53.6	42.0	59.3
BTX (gas phase) µg/g coal	1.8E4	2.1E4	4.2E3
PCX tar µg/g coal	12		2270
PCX cond. µg/g coal	42		670
PCX total µg/g coal	54		2900
Tar: acids %	0.6		30.96
bases %	2.2		2.57
insoluble %	32.6		2.00
NPN %	12.1		27.82
PNA %	46.8		18.54
PN %	5.5		18.10

BTX = benzene, toluene, xylene
PCX = phenol, cresols, xylenols
NPN = Nonpolar neutrals
PNA = Polynuclear aromatics
PN = Polar neutrals

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TABLE 3-3. COMPARISON OF OPERATING CONDITIONS, PRODUCT AND BYPRODUCT OUTPUTS

	Continuous		Semicontinuous
Feed	Montana Rosebud		Montana Rosebud
Test	C-3		25
Mesh	8 x 16		8 x 16
Pressure	210 psia		200 psia
Air/steam g/g	4.6		3.4
Carbon conversion %	100		99.7
S conversion %	97		85
N conversion %	99		99
Tar yield µg/g coal	4.4		18
Average max. temp.°C	990	1005	1006
Gas comp. %	overall	steady	
CH_4	2.4	2.4	2.4
CO	14.4	14.3	23.1
CO_2	13.2	13.4	8.5
H_2	8.9	8.8	15.7
N_2	61.0	61.0	50.3
BTX (gas phase) µg/g coal	≈1.2E4	1.2E4	6.9E3
PCX tar µg/g coal	4		260
PCX cond. µg/g coal	57		380
PCX total µg/g coal	61		640
Tar: acids %	0.3		11.1
bases %	1.6		4.8
insoluble %	51.9		2.8
NPN %	13.4		7.4
PNA %	30.5		68.7
PN %	2.3		5.2

BTX = benzene, toluene, xylene
PCX = phenol, cresols, xylenols
NPN = Nonpolar neutrals
PNA = Polynuclear aromatics
PN = Polar neutrals

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Operating conditions for the two test modes are consistent for a given coal feed with a few exceptions. Test C-1 was conducted at 115 psia, while test 43, to which it is compared, was conducted at 200 psia. The air/steam ratio in test C-2 was only two-thirds of that used in the test to which it is compared (test 47). A similar discrepancy exists between tests C-1 and 43.

For the continuous tests, a period of constant input and output conditions was identified during the time that the coal was being fed. This period commenced somewhat after the beginning of the test when a bed of char or ash was established in the reactor and conditions stabilized. For gas phase products and byproducts chemical analyses were available throughout the tests. Separate entries of these analyses for the constant period and for the overall test are given in Tables 3-1 through 3-3. Solid and liquid samples were composited throughout the tests and chemical analyses covering the entire test are given. Periods of constant conditions largely dominated these tests, however, so these samples mainly represent constant operation with a minor influence of start-up and shut-down effects.

Overall product gas compositions did not vary much from those measured during constant operation periods for the continuous tests. The increased overall nitrogen content of the product gas in test C-3 is due to operation of the gasifier from the time that all of the coal had been fed until oxygen was detected in the exit gas. On a nitrogen-free basis, the product gas from continuous tests was higher in CO_2 and lower in CO than the product gas from the semicontinuous tests. This would suggest that major product gas distributions were driven by a lower temperature in the continuous tests, although this was not observed in the case of time-averaged maximum bed temperature. Also, bed depths were lower in the continuous tests; this may have decreased the extent of reduction of carbon dioxide to carbon monoxide.

Very prominent differences between the continuous and semicontinuous tests were noted in several areas. Most significant were the large differences in phenolic production in the condensate and tar. The yield of phenolic material in the condensate, as measured by the sum of phenol, cresols, and xylenols was 6 to 40 times less in the continuous tests than the semicontinuous tests. In the nonaqueous tar phase, which was kept in contact with the condensate during the course of the test and for at least 24-hours after the test, the same trend was evident to a larger extent. Sixty-five to 400

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times less phenolic material was present in the tar from continuous tests than in the tar from the semicontinuous tests. This was due in part to the large difference in tar yield in the two operating modes (discussed below). A likely reason for these differences is the lower temperature at which devolatilization took place in the semicontinuous tests. Also, for the semicontinuous tests, the lower portion of the coal bed may have been exposed to oxidative conditions during the early stages of devolatilization, leading to greater production of oxygenated compounds.

A second significant difference between the continuous and semicontinuous modes of operation is the greatly reduced tar yield in the continuous tests. Tar yields in the semicontinuous tests were 1.5 to 47 times the tar yields in the continuous tests for the same coal type. Here again, it is thought that the lower devolatilization temperature in the semicontinuous tests was responsible. The lower temperatures may have promoted polymerization of lower molecular weight compounds.

Larger scale fixed-bed gasifiers, such as Lurgi and Chapman gasifiers, are commonly described as operating in the continuous feed mode but could be more accurately characterized as intermittent feed processes, because coal may be charged in the form of several discrete loads per hour. Such systems may operate intermediately between the continuous and semicontinuous modes of the laboratory gasifier since coal devolatilizes at a high temperature but the devolatilization products are concentrated during particular time intervals. Larger mesh coal feeds in some full-scale processes may also slow the heating rate appreciably and thus increase tar yields. A tar yield of 30 mg/g coal was reported[5] for a Lurgi gasifier operated with 1-3/4 x 1/4 inch Montana subbituminous coal, in contrast to yields of 18 and 4.4 mg/g coal obtained in the semicontinuous and continuous modes with the laboratory system.

Aside from the quantity of tar produced, the chemical and physical characteristics of the tars produced in the two operating modes differ. The results of a solvent fractionation of the tar indicated a greatly reduced proportion of tar acids in the continuous gasification tar for all three coal types as supported by the greatly reduced phenolic production. In addition, the continuous gasification tar contains a much higher proportion of cyclohexane insolubles than the tar from semicontinuous operation. The

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specific chemical analysis of this fraction has not been determined for any of the tests described, but a qualitative GC/MS scan of the cyclohexane insoluble fraction of another semicontinuous gasification tar showed it to be chiefly polynuclear aromatic hydrocarbons which were incompletely separated in the fractionation procedure. All of the material considered as tar in this investigation was soluble in methylene chloride, so the change in the proportion of cyclohexane insolubles cannot be ascribed to inorganic or flyash materials. If the cyclohexane insoluble fraction of the continuous gasification tar does in fact contain polynuclear aromatic hydrocarbons, this tar may be more hazardous on a unit basis than the tar from semicontinuous operation; the lower overall yield from continuous tests represents less of a handling and reuse problem, however.

A difference in gas phase aromatic content was noted between the two modes of operation with the BTX yield of the continuous tests being 1.7 to 4.7 times that of the semicontinuous tests. The reasons for this are possibly the same as those given for the decreased tar production in continuous tests. If the lower devolatilization temperatures in the semicontinuous test promoted polymerization of BTX molecules, this would result in an increased tar yield and a decreased BTX yield. If the overall yields of tar and BTX are combined, the production of this class of material compares much more closely between the two operating modes for a given coal type. This information is summarized in Table 3-4.

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TABLE 3-4. TAR AND BTX YIELDS FOR CONTINUOUS AND SEMICONTINUOUS OPERATING MODES (mg/g coal)

		overall continuous	semicontinuous
Montana	tar	4.4	18
	BTX	12	6.9
	TOTAL	16	25
Wyoming	tar	4.4	20.8
	BTX	18	4.2
	TOTAL	22	25
N. Dakota	tar	4.8	7.2
	BTX	6.6	1.4
	TOTAL	11	8.6

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4.0 EFFECT OF ADDITION OF ALKALI METALS

It has long been known that alkali metal compounds can catalyze the steam carbon reaction in gasification processes. Haynes et al.[1] found that addition of 5 percent (by weight) of alkali metal compounds to coal increased gasification rate by 31 to 66 percent. Kalina[2] reported that potassium carbonate prevents agglomeration of caking coals under gasification conditions. A review of the Fundamental Aspects of Catalyzed Coal Char Gasification has recently been published.[3] Although the catalytic effects of these additives have been investigated and at least one process has advanced to the pilot plant stage,[4] little research has been done to quantify the effects of these additives upon production of trace contaminants and byproducts of environmental significance.

Three catalytic gasification tests were conducted in the semicontinuous fixed-bed mode using Illinois No.6 bituminous coal to which alkali metal compounds had been added. The tests were conducted under similar operating conditions to earlier uncatalyzed Illinois No.6 gasification tests. All tests were continued until the carbon in the feed was substantially depleted; this was accompanied by a breakthrough of oxygen in the product gas in all tests except No.54. In test No.54 a mixture of 80 percent (wt) Illinois No.6 coal and 20 percent potassium carbonate was gasified. This mixture had a composition similar to that reported for the feed to the Exxon Catalytic Gasification Process.[4] In tests 56 and 58, a mixture of 98 percent (wt) Illinois No.6 coal and 2 percent sodium hydroxide was gasified.

The feed for the catalytic tests was prepared by drying 8 x 16 mesh Illinois No.6 coal to constant weight at 105°C. The desired mass of additive was dissolved in deionized water and mixed with the dried coal in Pyrex crystalizing dishes. Sufficient additional deionized water was added to the dishes to cover the coal, and the resulting slurries were mixed again. The dishes containing the slurries were then dried again to constant weight at 105°C. The individual coal particles in the feed for test No.56 tended

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to clump together during the drying process. These clumps were broken up manually prior to the test, and the entire feed was passed through a four mesh screen. Analyses of the feed as gasified are given in Table 4-1 for three catalytic tests and two noncatalytic tests conducted under similar conditions. Analyses of the gasification residues from these tests are given in Table 4-2.

Operating conditions for the five tests are given in Table 4-3. The system pressure, measured immediately before the back pressure regulator was approximately equal for all tests. Variations of ± 10 psi occurred in the course of the individual tests as a result of changing product gas flow rates and differences in the pressure drop through the coal bed. Pressures measured upstream of the flow distributor and coal bed were generally 5-10 psi higher than those reported in the table. The initial mesh size in each test was 8x16. The change in feed size for test No.54 is probably not significant because the feed material fused together in the reactor in all cases. Although catalyst treatment is reported to decrease caking properties under some conditions, this effect was not observed in the laboratory system. The ASTM[5] free-swelling index test did, however, reveal a reduction in FSI as a result of catalyst addition.

An important difference in operating procedure between tests 56 and 58 was the time of initial air addition. In tests 23, 44, 54, and 56, the flow of air to the reactor was started immediately following the introduction of the coal into the preheated reactor. For test 58, pyrolysis took place in the presence of steam and nitrogen for the first 20 minutes following the coal drop. This caused a slower heatup rate than that of test 56 or any of the other tests. Specifically, for test 58, during the 20-minute period prior to the addition of air, the maximum reactor temperature rose to 930°C as a result of heat input from the preheated reactor. A comparable increase in temperature for test 56 required only 10 minutes, using combustion heat as well as heat transferred from the preheated reactor.

The average maximum coal bed temperature varied between 976° and 1037°C. This is thought to be strongly influenced by channeling within the coal bed. The materials of the reactor imposed a maximum allowable temperature of about 1050°C; when this temperature was reached, the air flow rate was decreased. Such decreases were required in all tests irrespective of

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TABLE 4-1. RAW FEED ANALYSES - AS GASIFIED

Test	Noncatalytic	Catalytic		
	23 and 44	54	56	58
Proximate				
Moisture, %	5.31	1.85	1.50	1.27
Ash, %	11.03	26.73	16.22	11.04
Volatile matter, %	34.16	1.94	31.42	34.05
Fixed carbon, %	49.50	69.48	50.86	53.64
Ultimate				
Moisture, %	5.31	1.85	1.50	1.27
Ash, %	11.03	26.73	16.22	11.04
Carbon, %	66.35	55.95	63.85	65.90
Hydrogen, %	4.73	3.35	4.38	4.26
Nitrogen, %	1.52	1.39	1.51	1.47
Chlorine, %	0.30	0.26	0.30	0.09
(Pyritic sulfur), %	(1.24)	(0.78)	(1.07)	(1.18)
(Organic sulfur), %	(1.83)	(1.15)	(1.21)	(1.18)
(Sulfate sulfur), %	(0.00)	(0.16)	(0.20)	(0.18)
Total sulfur, %	3.07	2.09	2.48	2.54
Oxygen, %	7.69	8.38	9.76	13.43
Heating value (Btu/lb)	11952	9478	11284	11289
Free swelling index	3.5	0.5	1.0	0.5
Mass charged (g)	1594, 1246	1261	1264	1325

TABLE 4-2. RESIDUE ANALYSES

Test	Noncatalytic		Catalytic		
	23	44	54	56	58
Proximate					
Moisture %	0.68	7.14	5.94	1.15	3.53
Ash, %	82.37	53.98	89.31	68.72	96.09
Volatile matter, %	6.58	5.52	2.56	3.36	0.27
Fixed carbon, %	10.37	33.36	2.19	26.77	0.11
Ultimate					
Moisture, %	0.68	7.14	5.94	1.15	3.53
Ash, %	82.37	53.98	89.31	68.72	96.09
Carbon, %	15.57	35.95	0.35	27.59	0.12
Hydrogen, %	0.53	0.54	0.22	0.53	0.08
Nitrogen, %	0.57	0.33	0.14	0.37	0.10
Chlorine, %	NA	0.32	0.55	0.00	0.03
(Pyritic sulfur), %	(0.25)	(0.27)	(0.06)	(0.13)	(0.13)
(Organic sulfur), %	(0.40)	(0.14)	(0.21)	(1.14)	(0.40)
(Sulfate sulfur), %	(0.27)	(0.82)	(3.21)	(0.20)	(0.67)
Total sulfur, %	0.92	1.23	3.48	1.47	1.20
Oxygen, %	--	0.51	0.01	0.17	0.05
Heating value (Btu/lb)	2263	5368	137	4291	4
Residue mass (g)	261	252	318	242	173

TABLE 4-3. GASIFIER OPERATING CONDITIONS

Test	Noncatalytic		Catalytic		
	23	44	54	56	58
Feed material	Illinois No.6	Illinois No.6	Illinois No.6	Illinois No.6	Illinois No.6
Catalyst	none	none	K_2CO_3	NaOH	NaOH
Coal g	1594	1246	1009	1239	1309
Catalyst g	zero	zero	252	24.8	26.2
Air g	3288	4753	3504	3463	2902
Steam g	1952	1084	596	755	952
Pressure psia	200	200	210	200	200
Mesh	8 x 16	8 x 16	8 x 16*	8 x 16	8 x 16
Test length min	297	271	267	329	216
Mean maximum temp °C	1021	976	NA	1037	1010
Carbon conversion %	96	89	99.8	92	100
Sulfur conversion %	95	92	58	89	94
Nitrogen conversion %	94	96	97	95	99

*Material agglomerated during catalyst application and was reduced to -4 mesh before loading.
NA=not available.

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catalytic treatment. The zone of maximum temperature usually occurred somewhat above the flow distributor immediately after the coal was introduced, and moved downward to the flow distributor shortly afterward. As the tests progressed, this zone then moved upward through the coal bed as the carbon was depleted.

Based on reports in the literature, catalytic treatment was expected to increase the rate of the steam-carbon gasification reaction. This reaction is highly endothermic and is driven by the exothermic combustion reaction. The effect of this catalysis would be a lowered reaction temperature; such an effect was not observed. Additionally, no effect upon the overall rate of reaction as measured by the test length was noted. As the test length reflected the time necessary for essentially complete reaction of the carbon in the coal (accompanied by breakthrough of unreacted oxygen in all cases but test 54), a substantially increased overall rate should have been accompanied by a shorter test length. No evidence of this effect was found.

From the environmental standpoint, the most significant result of catalytic treatment was the low sulfur conversion observed in test 54. Sulfur conversion, the fraction of sulfur present in the feed material that was not accounted for in the solid residue, was only 58 percent for the K_2CO_3 treated material. This contrasts with sulfur conversions of 92 percent and 95 percent for the noncatalytic tests and 89 percent and 94 percent for the two NaOH catalyzed tests. For the K_2CO_3 catalyzed test, 42 percent of the sulfur was retained in the residue even though over 99 percent of both the carbon and higher heating value of the feed material was removed. Thus, K_2CO_3 addition may represent a pollution control option for the reduction of gaseous sulfur compounds. It should be noted that the NaOH treatment did not affect sulfur conversion; this may be due to the much lower amount used, or to differences in, chemical interactions.

Product gas compositions are reported in Table 4-4. In the catalytic tests, a much greater amount of CO relative to CO_2 was produced than in the noncatalytic tests. This effect was observed both for the K_2CO_3-treated coal and the NaOH-treated coal. This product shift is typically associated with higher reaction temperatures; however, this could not be accounted for by the observed time-averaged maximum reactor temperatures. Time-averaged

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TABLE 4-4. PRODUCT GAS COMPOSITIONS (MOISTURE-FREE BASIS)

Test	Noncatalytic		Catalytic		
	23	44	54	56	58
CH_4 %	3.1	2.6	2.1	2.8	2.4
CO %	10.0	6.0	19.0	19.4	21.4
CO_2 %	18.0	15.5	11.0	7.8	8.8
H_2 %	13.0	8.8	9.3	13.4	18.9
Balance* %	55.9	67.1	58.6	56.6	48.5
Volume (m^3)	5.7	4.7	4.2	4.5	5.1
BTX (µg/g coal)	9.0E3	6.8E3	8.0E3	7.3E3	6.0E3
H_2S (µg/g coal)	1.9E4	2.0E4	8.5E3	2.1E4	2.4E4
H_2S (µg/g sulfur in)	6.2E5	6.7E5	3.3E5	8.3E5	≈1.0E6
H_2S/COS (v/v)	320	46	61	17	22

BTX = benzene + toluene + xylenes + ethylbenzene
*principally nitrogen, also includes sulfur compounds and C_{2+} hydrocarbons

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mean reactor temperatures, approximately 910° and 820°C for the noncatalytic tests 23 and 44 as opposed to 880° and 910°C for the catalytic tests 56 and 58, also failed to support the shift in product gas composition. These numbers are much less accurate than the time-averaged maxima, however, as swelling and collapse of the coal bed and channeling of reactant gases make the average coal temperature difficult to estimate. Gas compositions and yields pertain to the total product gas, integrated from the time that the coal was added to the reactor until the end of the test.

The catalytic treatment failed to result in a consistent change in the light aromatic yield. While the H_2S yield was unaffected by the 2 percent NaOH treatment, it was substantially reduced by the 20 percent K_2CO_3 treatment. This is consistent with the previously discussed effect of increased sulfur retention in the residue. H_2S yields have been reported both on an input coal basis and on an input sulfur basis. Calculations for test 58 show slightly greater H_2S production than that associated with complete conversion of input sulfur to H_2S. This is probably due to inaccuracies in the flow-averaging procedure used to determine the total H_2S yield from a number of discrete observations. Accounting for the sulfur retained in the ash and tar, and that converted to COS, the H_2S yield should be approximately 90 percent of the sulfur in the feed coal.

The ratio of H_2S to COS, important in the design and selection of gas cleaning processes, was not consistently affected by the catalytic treatment. In addition, no consistent effect upon the approach to pseudoequilibrium of the reaction $H_2 + COS \longrightarrow H_2S + CO$ could be attributed to the catalytic treatment. (As the gas compositions reported are those calculated by flow-averaging discrete measurements over the course of the semicontinuous tests, equilibrium would not be expected.)

Tar yields and compositions are shown in Table 4-5. During test 56, in which NaOH-treated coal was gasified, much less tar was produced than in any of the other tests. Test 58, which was conducted with the same feed material as test 56, produced over twice as much tar, but this may have been due to the slower heating rate and delayed air input. Although the K_2CO_3-treated coal yielded slightly less tar than the noncatalyzed coal, additional testing would be necessary to determine if this reduction is significant. The result of a tar partition scheme, described in an earlier

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TABLE 4-5. TAR YIELD AND COMPOSITION

Test	Noncatalytic		Catalytic		
	23	44	54	56	58
Tar yield: (mg/g coal)	32.8	24.1	22.5	9.5	19.9
Tar partition:					
Acids %	12.9	6.5	14.1	17.8	22.1
Bases %	7.2	6.5	6.1	5.3	7.0
Cyclohexane insoluble %	11.3	4.8	3.4	2.6	7.7
Nonpolar neutral %	11.1	11.2	14.6	16.3	28.5
Polynuclear aromatic %	53.6	67.4	36.9	54.6	24.1
Polar neutral %	4.0	3.6	25.0	3.4	10.5
Tar composition:					
C %	86.01	NA	65.53	86.34	NA
H %	5.78	NA	5.48	6.10	NA
N %	1.61	NA	1.44	1.57	NA
S %	2.53	NA	1.52	2.70	NA
O %	3.80	NA	4.33	2.85	NA

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report,[6] shows that both the NaOH and K_2CO_3 treatments increased the proportion of acids and nonpolar neutrals. The K_2CO_3 treatment may have reduced the polynuclear aromatic fraction; such a reduction would be desirable, as some of the most hazardous compounds found in the tar, such as benzo(a)pyrene, are associated with this fraction.

Elemental analyses revealed no significant difference between the tar produced in noncatalytic gasification test 23 and the tar produced in the NaOH-treated coal gasification test 56. The elemental analysis of tar produced in noncatalytic gasification test 23 and the tar produced in the NaOH-treated coal gasification test 56. The elemental analysis of tar produced in test 54 is probably incorrect; the deficiency in this analysis may have been caused by incomplete removal of the solvent, methylene chloride, from the sample submitted for analysis. If this analysis is normalized to 100 percent, the elemental composition of tar resulting from gasification of the K_2CO_3-treated coal does not vary widely from that of the noncatalytic gasification tar or from the tar produced during gasification of NaOH-treated coal.

In conclusion, the results of fixed-bed, semicontinuous air-blown gasification tests of catalytically treated coal conducted in the RTI laboratory reactor showed that:

1. Catalytic treatment did not increase gasification rates.
2. Catalytic treatment did not substantially lower reaction temperatures.
3. Catalytic treatment did not decrease the caking and swelling tendencies of Illinois No.6 coal in the laboratory reactor, although it did reduce the free-swelling index as measured by the ASTM procedure.
4. Treatment with K_2CO_3 increased retention of sulfur in the solid residue and decreased production of H_2S in the product gas; treatment with NaOH (at a much lower level) did not produce this effect.
5. Catalytic treatment did not affect nitrogen retention in the solid residue.
6. Catalytic treatment increased the production of CO and decreased the production of CO_2.

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7. Treatment with NaOH reduced overall tar production.
8. Tars produced from catalytically treated coal had a greater proportion of acids and nonpolar neutrals than tars produced from untreated coal.
9. Tar produced from K_2CO_3-treated coal had a decreased proportion of polynuclear aromatic hydrocarbons than tar from untreated coal.
10. Elemental composition of tar produced from gasification of NaOH-treated coal did not differ from that of tar produced from gasification of untreated coal.

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5.0 EFFECTS OF PRESSURE AND MESH SIZE VARIATIONS

A series of experiments were conducted to assess the effects of variations of pressure and particle size upon gasification products and byproducts. Typically, gasification tests were conducted in the fixed-bed, semicontinuous air-blown mode, with 8x16 mesh coal at approximately 200 psia. For Illinois No.6 bituminous coal and North Dakota Beulah/Zap lignite, separate gasification tests were conducted at lower pressures and with larger mesh feed material than the typical base case. Analyses of the coal used in these tests and the residue after gasification are given in Tables 5-1 and 5-2.

Aside from the deviations in pressure and mesh size, operating conditions were held as closely as possible to those of the base case. The lower pressure tests were conducted with reduced input rates for air and steam to partially compensate for the reduced gas residence times resulting from lower pressure operation. Since the lower pressure tests required a longer time for substantially complete reaction of the feed, overall steam and air inputs are approximately equal to those in the base cases. Operating conditions for the Illinois No.6 tests--two base cases as well as the pressure variation test and the mesh size variation test--are given in Table 5-3. Similar information for the North Dakota lignite tests is given in Table 5-4.

All tests except for test 50 were continued until oxygen was detected in the product gas. Test 50 was terminated when substantially all of the carbon in the feed was depleted. For each coal type the lower pressure tests took longer than the base case test because of reduced air and steam input rates. Carbon and nitrogen conversions were uniformly high for the North Dakota lignite tests, while sulfur conversion varied from 65 to 97 percent without apparent dependence on pressure or mesh size. For the Illinois No.6 coal tests, carbon, nitrogen, and sulfur conversions for individual tests were roughly equivalent, with conversions slightly lower in the larger mesh test.

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TABLE 5-1. RAW COAL ANALYSES FOR PRESSURE AND MESH SIZE EXPERIMENTS

Test	Illinois No.6 Coal		N. Dakota Zap Lignite
	23, 44 and 50	52	36, 43, 49 and 51
Proximate			
Moisture, %	5.31	5.97	29.63
Ash, %	11.03	10.40	6.39
Volatile matter, %	34.16	33.99	28.57
Fixed carbon, %	49.50	49.64	35.41
Ultimate			
Moisture, %	5.31	5.97	29.63
Ash, %	11.03	10.40	6.39
Carbon, %	66.35	66.27	46.82
Hydrogen, %	4.73	4.61	6.56
Nitrogen, %	1.52	1.52	0.73
Chlorine, %	0.30	0.33	0.02
(Pyritic sulfur), %	(1.24)	(0.82)	(<0.01)
(Organic sulfur), %	(1.83)	(1.69)	(0.54)
(Sulfate sulfur), %	(0.00)	(0.09)	(0.02)
Total sulfur, %	3.07	2.60	0.56
Oxygen, %	7.69	8.30	9.29
Heating value (Btu/lb)	11952	11758	7880
Free swelling index	3.5	4	0

TABLE 5-2. RESIDUE ANALYSES: PRESSURE AND MESH SIZE EXPERIMENTS

Test	Illinois No.6 Coal				North Dakota Zap Lignite			
	Base Case 23	44	Pressure Variation 50	Mesh Variation 52	Base Case 36	43*	Pressure Variation 49**	Mesh Variation 51***
Proximate								
Moisture %	0.68	7.14	10.36	0.77	3.76	4.69	0.57	0.23
Ash %	82.37	53.98	66.06	56.73	91.99	88.51	86.99	95.87
Volatile matter %	6.58	5.52	4.81	2.56	1.59	14.38	16.02	2.60
Fixed carbon %	10.37	33.36	18.77	39.94	2.66	--	--	1.30
Ultimate								
Moisture %	0.68	7.14	10.36	0.77	3.76	4.69	0.57	0.23
Ash %	82.37	53.98	66.06	56.73	91.99	88.51	86.99	95.87
Carbon %	15.57	35.95	20.84	39.61	2.52	5.24	15.00	0.10
Hydrogen %	0.53	0.54	0.58	0.50	0.15	1.63	0.42	0.01
Nitrogen %	0.57	0.33	0.53	0.72	0.06	0.00	0.48	0.05
Chlorine %	NA	0.32	0.04	0.06	0.08	0.09	0.09	0.04
(Pyritic sulfur) %	(0.25)	(0.27)	(0.03)	(0.06)	(0.15)	(0.06)	(1.02)	(0.06)
(Organic sulfur) %	(0.40)	(0.14)	(0.22)	(1.49)	(0.08)	(0.44)	(3.05)	(0.69)
(Sulfate sulfur) %	(0.27)	(0.82)	(1.03)	(0.01)	(0.80)	(1.71)	(0.01)	(2.94)
Total sulfur %	0.92	1.23	1.28	1.56	1.03	2.21	4.08	3.69
Oxygen %	--	0.51	0.31	0.05	0.41	--	--	0.01
Heating value (Btu/lb)	2263	5368	3145	6321	309	544	2165	30
Residue mass (g)	261	252	382	399	71.6	129	69.7	59.2

*CO_2 = 2.69%; 10 g sample leached with 1:6 HCl yielded 3 g solids.

**CO_2 = 4.43%.

***CO_2= 0.75%; CO_2 of residue from volatile matter test = 0.47%.

TABLE 5-3. GASIFIER OPERATING CONDITIONS - ILLINOIS NO.6 COAL

Test	Base Case		Lower Pressure	Larger Mesh
	23	44	50	52
Coal Type	Illinois #6	Illinois #6	Illinois #6	Illinois #6
Pressure psia	200	200	40	200
Mesh	8x16	8x16	8x16	4x8
Coal g	1594	1246	1649	1637
Air g	3288	4753	4905	4734
Steam g	1952	1084	1206	1551
Test length min	297	271	548	323
Mean maximum temp °C	1021	976	978	1019
Carbon conversion %	96	89	93	85
Sulfur conversion %	95	92	89	85
Nitrogen conversion %	94	96	93	88

TABLE 5-4. GASIFIER OPERATING CONDITIONS - NORTH DAKOTA BEULAH/ZAP LIGNITE

Test	Base Case		Lower Pressure	Larger Mesh
	36	43	49	51
Coal Type	N.D. Lignite	N.D. Lignite	N.D. Lignite	N.D. Lignite
Pressure psia	205	200	50	210
Mesh	8x16	8x16	8x16	4x8
Coal g	1444	1458	1473	1491
Air g	1939	2022	1876	1856
Steam g	639	422	494	449
Test length min	136	96	225	102
Mean maximum temp °C	916	914	999	939
Carbon conversion %	99.7	99	99.6	100
Sulfur conversion %	91	65	97	74
Nitrogen conversion %	99.6	100	97	99.7

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Product gas compositions and yields for the Illinois No.6 and North Dakota lignite tests are shown in Tables 5-5 and 5-6. For both coal types, the fraction of CO produced relative to CO_2 is increased in the lower pressure tests. This may result from an increased contribution of the reaction:

$$C + CO_2 \rightarrow 2CO \qquad (1)$$

Also, at any stage of the lower pressure semicontinuous tests, a greater ratio of carbon to reactants will be present in the reactor at lower pressures resulting from the lower gas density. Thus, the reduction of carbon dioxide and other secondary reactions may be enhanced.

In the Illinois No.6 tests, the ratio of CO to H_2 as well as that of CO to CO_2 increased under lower pressure operation. This increase in CO/H_2 ratio may have been responsible for the observed decrease in the H_2S/COS ratio. No such increase in CO/H_2 ratio occurred in the low pressure North Dakota lignite test, and no corresponding decrease in H_2S/COS ratio was observed. Lower pressure operation resulted in a very slight increase in H_2S yield for both feeds and a slight decrease in BTX yield for the Illinois No.6 test. Neither of these effects should be considered significant without further verification.

Larger mesh feed tests also produced an increased CO/CO_2 ratio for both feeds. There is no apparent explanation for this phenomenon; in fact, an opposite effect would be expected. For the Illinois No.6 coal, the larger mesh feed also produced an increased CO/H_2 ratio which was accompanied by a decreased H_2S/COS ratio. Neither change was observed in the North Dakota coal tests. For the Illinois No.6 coal, caking and swelling would be expected to reduce but not entirely eliminate the effects of feed size. Examination of residues from Illinois No.6 gasification test revealed that although the particles were fused together, individual particles could still be identified.

The larger mesh Illinois No.6 test produced slightly less benzene, toluene, and xylenes (BTX) than the base case; this did not occur in the larger mesh North Dakota lignite test. The larger mesh North Dakota lignite test produced slightly more H_2S than the base case; this did not occur in the larger mesh Illinois No.6 test. Overall, it is possible that no significant effect upon the product gas composition resulted from a doubling of particle size.

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(4-76)

TABLE 5-5. PRODUCT GAS COMPOSITIONS (MOISTURE-FREE BASIS) - ILLINOIS NO.6 COAL

Test	Base Case		Lower Pressure	Larger Mesh
	23	44	50	52
CH_4 %	3.1	2.6	2.1	2.6
CO %	10.0	6.0	12.4	13.2
CO_2 %	18.0	15.5	13.5	12.2
H_2 %	13.0	8.8	10.5	8.6
Balance* %	55.9	67.1	61.5	63.4
Volume (m^3)	5.7	4.7	5.4	4.3
BTX (µg/g coal)	9.0E3	6.8E3	6.4E3	5.0E3
H_2S (µg/g coal)	1.9E4	2.0E4	2.1E4	1.6E4
H_2S (µg/g sulfur in)	6.2E5	6.7E5	6.8E5	6.2E5
H_2S/COS (v/v)	320	46	30	19

BTX = benzene + toluene + xylenes + ethylbenzene
*principally nitrogen, also includes sulfur compounds and C_{2+} hydrocarbons

TABLE 5-6. PRODUCT GAS COMPOSITIONS (MOISTURE-FREE BASIS) - NORTH DAKOTA BEULAH/ZAP LIGNITE

Test	Base Case		Lower Pressure	Larger Mesh
	36	43	49	51
CH_4 %	1.5	2.4	2.4	3.8
CO %	20.0	21.0	25.6	26.0
CO_2 %	9.6	8.7	8.5	5.8
H_2 %	17.0	13.0	20.7	18.0
Balance* %	51.9	54.9	42.8	46.4
Volume (m^3)	3.3	3.2	3.0	2.4
BTX (µg/g coal)	7.3E3	3.4E3	5.9E3	6.7E3
H_2S (µg/g coal)	2.3E3	1.7E3	2.4E3	2.6E3
H_2S (µg/g sulfur in)	4.1E5	3.0E5	4.3E5	4.6E5
H_2S/COS (v/v)	25	11	19	25

BTX = benzene + toluene + xylenes + ethylbenzene
*principally nitrogen, also includes sulfur compounds and C_{2+} hydrocarbons

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Tar yields and compositions for Illinois No.6 coal and North Dakota Beulah/Zap lignite tests are shown in Tables 5-7 and 5-8. Lower pressure operation resulted in greatly increased tar production from Illinois No.6 coal. This tar had a much higher percentage of acids (chiefly phenolics) and a lower percentage of polynuclear aromatic hydrocarbons than the tar produced at higher pressure. Corresponding to the increase in acids, an increased oxygen content was found in the tar. The increased tar yield may be due to the lower partial pressure of hydrogen which promotes cracking of ring structures. Silsby and Sawyer[1] reported a one-half order dependence of cracking upon hydrogen concentration in aromatic cracking experiments. This explanation fails to explain the fact that the tar yield from North Dakota lignite gasification tests was unaffected by lower pressure operation. The effects upon the composition of tar produced in lower pressure gasification do correspond between the two coal types tested. An increased fraction of acids, accompanied by an increased oxygen content in the tar, was found to result from lower pressure gasification of North Dakota lignite. Additionally, the decreased production of polynuclear aromatic hydrocarbons was also observed. Finally, the North Dakota low pressure gasification tar had a lower fraction of bases than the high pressure tar. This is confirmed by a decreased nitrogen content in the tar, as most of the compounds identified to date in the tar base fraction are nitrogen-containing compounds such as quinolines, acridines, and indoles.

The tar yield from gasification of larger particles increased by about 50 percent over the base cases for North Dakota lignite. No change in tar yield with mesh was found for Illinois No.6 coal. Larger mesh particles would be expected to experience a slower heating rate following introduction to the reactor as a result of increased resistence to conductive heat transfer. A lower devolatilization temperature may have been responsible for the increased tar yield resulting from gasification of a larger mesh coal. The swelling and partial fusion of the Illinois No.6 coal may have diminished the effect of particle size on devolatilization temperature.

The tar produced from gasification of the larger mesh Illinois No.6 coal had a greater proportion of acids (accompanied by increased oxygen content) and a decreased proportion of bases (accompanied by a decreased nitrogen content). Additionally, a lower proportion of polynuclear aromatic

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(4-76)

TABLE 5-7. TAR YIELD AND COMPOSITION - ILLINOIS NO.6 COAL

Test	Base Case		Lower Pressure	Larger Mesh
	23	44	50	52
Tar yield: (mg/g coal)	32.8	24.1	56.4	30.1
Tar partition:				
Acids %	12.9	6.5	17.5	19.8
Bases %	7.2	6.5	7.7	2.7
Cyclohexane insoluble %	11.3	4.8	11.6	9.0
Nonpolar neutral %	11.1	11.2	29.8	16.8
Polynuclear aromatic %	53.6	67.4	24.2	44.6
Polar neutral %	4.0	3.6	9.1	7.2
Tar composition:				
C %	86.01	NA	84.08	85.52
H %	5.78	NA	6.78	6.50
N %	1.61	NA	1.14	1.04
S %	2.53	NA	1.55	1.87
O %	3.80	NA	6.09	4.87

NA = Not Available

TABLE 5-8. TAR YIELD AND COMPOSITION - NORTH DAKOTA BEULAH/ZAP LIGHNITE

Test	Base Case		Lower Pressure	Larger Mesh
	36	43	49	51
Tar yield: (mg/g coal)	8.3	7.2	8.1	11.9
Tar partition:				
Acids %	19.03	25.28	28.0	23.5
Bases %	5.09	5.42	3.2	4.5
Cyclohexane insoluble %	3.00	5.66	8.8	11.0
Nonpolar neutral %	14.79	20.70	23.4	17.1
Polynuclear aromatic %	52.14	33.21	25.4	36.2
Polar neutral %	5.95	9.73	11.2	7.7
Tar composition:				
C %	86.08	82.32	81.69	82.86
H %	7.04	7.51	7.74	6.92
N %	1.25	1.76	0.89	0.98
S %	0.69	0.94	1.06	2.51
O %	4.95	7.03	8.39	6.48

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hydrocarbons was found. No explanation for the change in composition of tar produced from larger mesh coal is available at this time. The tar produced from gasification of larger mesh North Dakota lignite is quite similar in solvent fractionation to the tar produced in the base cases. On an elemental basis it contains about three times as much sulfur as the tar produced in the base case tests. This sample was reanalyzed and the analysis was confirmed. As a greater H_2S yield was also observed for this large mesh North Dakota lignite test, it is possible that the raw coal feed used for this test was not adequately characterized by the batch analysis. Further experimental work would be required to determine the significance of coal mesh size on sulfur content in gasification tars.

The following observations were made, although their explanations and significance remain in doubt.

1. Gasification of larger particles produced a higher ratio of CO to CO_2.
2. Gasification of larger mesh Illinois No.6 coal produced a higher CO to H_2 ratio, a lowered H_2S to COS ratio, and a decreased yield of BTX. In addition, the tar produced was higher in acids and lower in bases and PNAs.
3. Gasification of larger mesh North Dakota lignite resulted in a higher yield of H_2S and an increased yield of tar with a higher sulfur content.
4. Lower pressure gasification (40-50 psia) resulted in a higher CO to CO_2 ratio and yielded tar with a higher fraction of acids and a lower fraction of PNAs than higher pressure gasification (200-205 psia).
5. Lower pressure gasification of Illinois No.6 coal resulted in a higher CO to H_2 ratio, a lower H_2S to COS ratio, and a greatly increased tar yield.
6. Lower pressure gasification of North Dakota lignite produced a tar containing a lower fraction of bases than the tar from higher pressure gasification.

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1. Silsby, R. I., and E. W. Sawyer. The Dealkylation of Alkyl Aromatic Hydrocarbons--I. The Kinetics and Mechanism of Toluene Decomposition in the Presence of Hydrogen. J. Appl. Chem., 6(347), 1956.
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6.0 EFFECTS OF COAL TYPE ON YIELDS OF POLLUTANTS AND BYPRODUCTS

The laboratory gasifier was operated in the semicontinuous, air-blown, fixed-bed mode with different eastern and western U.S. coals, ranging in rank from lignite to anthracite. For the base case of 200 psi, 8x16 mesh particles of North Dakota Beulah/Zap lignite, Montana Rosebud/McKay and Wyoming Smith/Roland subbituminous, Illinois No.6 and W. Kentucky No.9 bituminous, and Pennsylvania Bottom Red Ash Anthracite were gasified. Operating conditions varied somewhat among the tests, dictated in part by the differing reactivities. Operating data for the 13 tests considered in this section are given in Table 6-1.

The production of aromatic byproducts was found to be strongly dependent on coal type and rank. Several measures of aromatic production are shown in Figure 6-1. Tar yields are seen to increase with increasing rank, with subbituminous coals producing about twice as much tar as lignite and bituminous coals producing over three times as much tar as lignite. This trend is inconsistent with data reported for the Lurgi process,[1] an oxygen-blown fixed-bed gasifier which operates at higher pressures than the laboratory system. This trend is also inconsistent with data reported for the Wellman-Galusha gasifier[2] although when operated with anthracite coal, the Wellman-Galusha like the RTI gasifier produced no tar.

Phenol, cresols, and xylenols (PCX) were individually quantitated in the product gas, aqueous condensate, and tar that were produced in the gasification tests. The partitioning of these compounds into the three phases is thought to be influenced by the temperature and residence time in the condensate trap, which was difficult to control and varied from test to test. The total yield of these compounds recovered in the three phases should provide a more meaningful comparison between coal types and ranks (Figure 6-1). It can be seen that, with the exception of one Montana subbituminous test, the total yield of PCX declined with increasing coal rank, with the western coals producing almost twice as much PCX as the

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TABLE 6-1. OPERATING DATA--AIRBLOWN, FIXED BED, SEMICONTINUOUS GASIFICATION OF 8 x 16 MESH COAL AT 200 PSI

Coal Type	(Test)	Reactants (g)			Conversions (%)			Gas Yield (SCF/lb. MAF Coal)	Test Length Min
		Steam	Air	Coal	C	N	S		
N.D. Lignite	(36)	639	1939	1444	99.7	99.6	91	56.8	136
	(43)	422	2022	1458	99.0	100	65	55.2	96
Montana Sub.	(25)	748	2482	1491	99.7	85	99	54.9	180
Wyoming Sub.	(32)	500	2073	1360	99.5	95	92	41.7	121
	(33)	500	2097	1396	99.8	98	91	44.5	116
	(35)	521	2461	1420	97	95	84	51.4	116
	(47)	529	2288	1430	98	94	94	42.7	44
Illinois Bit.	(16)	3704	1350	1569	89	96	93	50.0	270
	(20)	3672	1368	1578	85	89	87	43.4	268
	(21)	4713	1720	1543	97	95	98	49.7	344
	(23)	1952	3288	1594	96	94	95	68.7	297
W. Ken. Bit.	(41)	1390	3060	1250	99.8	99.4	98	71.8	347
PA. Anth.	(48)	2844	7684	1847	84	85	89	83.6	233

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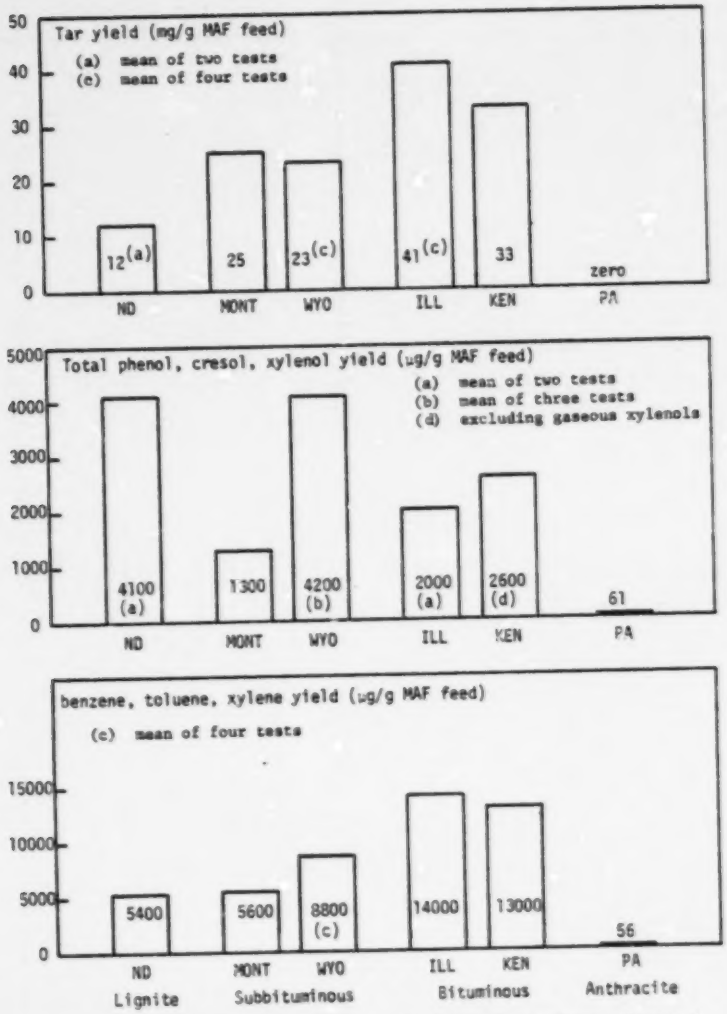

Figure 6-1. Effect of rank on byproduct production from airblown, fixed-bed, semicontinuous gasification of 8x16 mesh coal at 200 psi.

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eastern bituminous coals. The anthracite coal, which was low in oxygen and volatile matter, produced no tar and very little PCX in the product gas and aqueous condensate.

Benzene, toluene, and xylene (BTX) were measured in the product gas only. On the basis of GLC distillation data it is unlikely that a signifi cant quantity of these compounds was present in the tar phase. Tars from four N.D. lignite tests (including test 36), as well as Wyoming subbituminous test 47, contained no material which boiled below 150°C. Tars from three Illinois No.6 tests, other than the ones considered in this section, contained no material which boiled below 100°C. An average of 1.2 percent (by weight) of these tars boiled below 150°C. While these tars were produced under somewhat different operating conditions than the tests considered in this section, their chemical composition was similar. Thus it is likely that the gaseous BTX represents substantially all of the BTX produced.

Gaseous BTX yield is plotted as a function coal type and rank in Figure 6-1. This yield increases with increasing rank from lignite to bituminous. Gasification of anthracite produced about two orders of magnitude less BTX than the other coals. The trend from lignite to bituminous was inconsistent with that reported for the SYNTHANE process,[3] an oxygen-blown fluidized bed system. For the air-blown SYNTHANE process,[4] BTX yields were not monotonic with rank; Montana Rosebud subbituminous coal produced more BTX than either N.D. lignite or Illinois No.6 bituminous coal.

The tars produced in the gasification tests were characterized through a solvent-partitioning scheme[5] and also by elemental analysis. These analyses are shown in Table 6-2. The acid fraction is chiefly composed of phenolic compounds and generally accounts for a greater proportion of the western (lignite and subbituminous coal) tars than the eastern bituminous coal tars. This is consistent with the higher PCX yield and with the higher oxygen content of these coals. Bases made up a higher proportion of the tars from bituminous coals than of the tars from other coals. This fraction is composed chiefly of nitrogen-containing compounds such as aniline, indole, and quinoline derivatives. Of the remaining neutral fractions only the cyclohexane insolubles were strongly dependent on coal rank, making up a much larger proportion of the bituminous coal tars than the tars from lower rank coals.

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EPA-287 (Rev.) (4-76)

TABLE 6-2. COMPOSITION OF BYPRODUCT TAR FROM AIRBLOWN, FIXED BED, SEMICONTINUOUS GASIFICATION OF 8 x 16 MESH COAL AT 200 PSIG

	North Dakota Beulah/Zap Lignite	Montana Rosebud/McKay Subbituminous	Wyoming Smith/Roland Subbituminous	Illinois No.6 Bituminous	W. Kentucky No.9 Bituminous
Fractionation (%):	(a)		(c)	(c)	
acids	22.2	11.1	25.6	12.5	5.2
bases	5.3	4.8	3.6	6.6	7.1
cyclohexane insoluble	4.3	2.8	3.5	11.9	8.1
nonpolar neutral	17.7	7.4	20.8	16.9	12.5
polynuclear aromatic	42.7	68.7	36.3	46.1	61.7
polar neutral	7.8	5.2	10.2	6.0	5.4
Elemental Analysis (%):	(a)		(b)	(b)	
carbon	84.20	88.60	83.62	87.09	86.34
hydrogen	7.28	5.96	7.17	6.01	6.10
nitrogen	1.51	0.84	1.14	1.70	1.57
sulfur	0.82	0.71	1.47	1.97	2.70
oxygen	6.01	4.02	6.49	3.09	2.85

Note: Pennsylvania Bottom Red Ash Anthracite was also gasified in the same mode but did not produce any tar.

(a) mean of two tests
(b) mean of three tests
(c) mean of four tests

On an elemental basis the tars produced from all five coals were similar, with carbon-to-hydrogen ratios (weight) of 11.6 to 14.9. These ratios cover approximately the same range as the model compounds benzene (C/H = 12) and naphthalene (C/H = 15). As mentioned above, the oxygen content of the tars reflects the proportion of acids from the fractionation procedure. The sulfur content of the tar was dependent upon the sulfur content in the coal, which was between 0.6 and 0.8 weight percent (dry) for the western coals, as opposed to 3.24 percent for the Illinois No.6 and 4.78 percent for the W. Kentucky No.9.

The extent of sulfur conversion to different byproducts is shown in Table 6-3. In most cases, it was impossible to account for the entire sulfur input. These deficiencies are thought to result chiefly from failure to account for rapid evolution of gaseous sulfur species immediately following the introduction of coal into the preheated reactor. Overall material balances for sulfur and other elements have been previously reported.[6] In two of the tests considered in this section (16 and 23), slight excesses in sulfur were recovered as measured hydrogen sulfide concentrations accounted for greater than 100 percent of the input sulfur.

Sulfur concentrations were strongly dependent on the sulfur content of the coal used and consequently on the coal type. Data in Table 6-3 have been normalized with respect to coal input and the volumes of the product gas and effluent streams. Hydrogen sulfide production accounted for the greatest proportion of input sulfur. The Illinois No.6 bituminous and Pennsylvania anthracite coals had the highest H_2S yields, although this may be an artifact of sampling and analysis. Carbonyl sulfide, the other major gaseous sulfur compound produced, accounted for a maximum of 7 percent of the sulfur input; this occurred in the anthracite test. Overall, between 10 and 300 times as much sulfur was converted to H_2S as COS. The highest H_2S/COS ratios occurred for the Illinois No.6 coal tests, but this may be more a function of the high steam-to-air ratios (see Table 6-1) used in these tests than the type of coal.

The sulfur content of the aqueous condensate from several tests was determined. For a Montana subbituminous test, 7.5 percent of the total sulfur input was dissolved in the condensate. The amount of sulfur found in the condensate would be affected by the condensate production per mass

TABLE 6-3. SULFUR CONVERSION AND RETENTION IN AIRBLOWN, FIXED BED, SEMICONTINUOUS GASIFICATION OF 8 x 16 MESH COAL AT 200 PSI (μg/g sulfur input)

Feed	(Test No.)	H_2S Production	COS Production	Aqueous Sulfide	Tar Sulfur	Residue Sulfur
N.D. Lignite	(36)	4.1E5	3.1E4	NA	1.0E4	9.1E4
	(43)	3.0E5	5.2E4	NA	1.2E4	3.5E5
	average	3.6E5	4.2E4	NA	1.1E4	2.2E5
Montana Sub.	(25)	3.9E5	1.3E4	7.5E4*	2.1E4	1.5E5
Wyoming Sub.	(32)	3.6E5	6.5E4	NA	NA	7.5E4
	(33)	2.4E5	2.0E4	NA	5.2E4	8.9E4
	(35)	5.8E5	3.1E4	NA	2.8E4	1.6E5
	(47)	3.8E5	3.8E4	2.2E2	5.6E4	5.7E4
	average	3.9E5	3.9E4	2.2E2	4.5E4	9.5E4
Illinois Bit.	(16)	>1.1E6	7.5E3	NA	1.9E4	7.2E4
	(20)	5.5E5	5.4E3	NA	NA	1.3E5
	(21)	6.8E5	4.2E3	4.2E4*	1.9E4	1.9E4
	(23)	>1.1E6	8.1E3	NA	2.7E4	4.9E4
	average	8.6E5	6.3E3	4.2E4*	2.2E4	6.8E4
W. Ken. Bit.	(41)	4.5E5	2.5E4	NA	1.8E4	1.6E4
PA. Anth.	(48)	7.7E5	1.3E5	1.5E3	0.0	1.1E5

NA = Not Available
* Total Sulfur

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of sulfur converted, the condensate pH, and the conditions of temperature and pressure under which the condensate was collected. In the Lurgi process, which employs a quench system, 4.2 percent of the input sulfur in Montana Rosebud coal was found as aqueous total sulfur at the inlet to the oil separator. The comparable conversion for Illinois No.6 coal was 4.9 percent.[1]

As mentioned previously, the sulfur content of the tar was influenced primarily by the sulfur content of the coal gasified. When overall conversions are considered, the tar generated from gasification of Wyoming subbituminous coal accounts for a greater proportion of input sulfur than the tars from gasification of other coals, with an average of 4.5 percent of the input sulfur being converted to sulfur in the tar. The tar from the other western coals contains slightly less of the input sulfur than the tar from eastern bituminous coals. These tars were not analyzed for individual organic sulfur compounds, but tars generated in other tests from the same western coals were quantitatively analyzed by GC-FPD[7] and found to be similar in composition. The sulfur compounds quantitated included benzenethiol, toluenethiol, and a number of benzothiophene derivatives.

The sulfur retention in the residue varied from less than 2 percent for Illinois No.6 test 21 to 35 percent in N.D. lignite test 43. Overall, for the western coals a greater proportion of the sulfur was retained in the ash than for the eastern bituminous coals. This is consistent with combustion behavior in which the sulfur retention in the ash has been found to be proportional to the ratios of CaO to Al_2O_3 and Na_2O to SiO_2 in the major element analysis of the ash.[8] The western coals (particularly the N.D. lignite) are high in calcium and sodium, the basic components of the ash, relative to aluminum and silica. In the anthracite coal test, 11 percent of the input sulfur was retained in the ash. While this is quite high relative to the bituminous tests and slightly higher than the sulfur retention in the average Wyoming subbituminous test, it is more likely due to an overall decrease in reactivity than to the mineral matter composition. The carbon conversion obtained in this test was 84 percent, the lowest of the tests considered, and indicative of the low reactivity of the feed.

The extent of conversion of nitrogen to different byproducts is shown in Table 6-4. Not much data are available regarding ammonia formation in the product gas or aqueous condensate. For tests where data were available,

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TABLE 6-4. NITROGEN CONVERSION AND RETENTION IN AIRBLOWN, FIXED BED, SEMICONTINUOUS GASIFICATION OF 8 x 16 MESH COAL AT 200 PSI (μg/g nitrogen input)

Feed	(Test No.)	Ammonia-N Gaseous	Ammonia-N Aqueous	Tar Nitrogen	Residue Nitrogen
N.D. Lignite	(36)	NA	NA	1.4E4	4.1E3
	(43)	NA	NA	1.7E4	0.0
	average	NA	NA	1.6E4	2.1E3
Montana Sub.	(25)	3.8E4	2.8E5	1.2E4	3.8E3
Wyoming Sub.	(32)	NA	NA	NA	9.5E4
	(33)	NA	NA	2.6E4	1.6E4
	(35)	NA	NA	1.1E5	5.5E4
	(47)	9.1E4	5.9E5	6.2E4	6.4E4
	average	9.1E4	5.9E5	6.6E4	5.8E4
Illinois Bit.	(16)	NA	NA	4.9E4	4.4E4
	(20)	NA	NA	NA	1.1E5
	(21)	NA	4.8E5	3.1E4	4.8E4
	(23)	NA	NA	3.5E4	6.1E4
	average	NA	4.8E5	3.8E4	6.6E4
W. Ken. Bit.	(41)	NA	NA	4.4E4	6.0E3
PA. Anth.	(48)	8.2E3	3.5E5	0.0	1.5E5

NA = Not Available

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up to 9 percent of the nitrogen present in the coal was recovered as ammonia in the product gas and up to 59 percent was recovered in the condensate. It is expected that a water scrubbing system would operate to transfer ammonia from the gas to the aqueous phase. For tests 47 and 48, total Kjeldahl nitrogen (TKN) analyses were conducted on the condensate. It was found that 88 percent and 78 percent, respectively, of the TKN was due to ammonia nitrogen. The balance, organic nitrogen, is thought to be present as low molecular weight amines.

The tar contained as much as 11 percent (test 35) of the nitrogen content of the input coal. Nitrogen recoveries in the tar were highest for the Wyoming subbituminous tests, although since the Wyoming coal had a very low nitrogen content, the nitrogen content of the tar was relatively low (see Table 6-2). The Montana Rosebud test (25) showed the lowest nitrogen recovery in the tar; although the coal had over three times as much nitrogen as the Wyoming coal, the tar from the Montana test had the lowest nitrogen content by mass. On a mass basis, the gasification tars are more concentrated in nitrogen than the coals from which they originated with the exception of the Montana Rosebud test.

The amount of nitrogen retained in the solid residue after gasification varied between zero and 15 percent of the nitrogen input. Nitrogen retention did not vary consistently with coal rank; the Wyoming subbituminous, Illinois No.6 bituminous, and Pennsylvania anthracite residues retained an average of 5.8 percent, 6.6 percent, and 15 percent of the input nitrogen, compared with retentions of less than 1 percent for the N.D. lignite, Montana subbituminous, and W. Kentucky bituminous coals. As with sulfur, the high nitrogen retention in the anthracite residue is more indicative of its low overall conversion than its composition. Illinois No.6 coal in test 20 showed an 11 percent nitrogen retention in the residue, but this test also had a relatively low carbon conversion as 15 percent of the carbon input was also left in the residue.

In conclusion, the following effects of coal type on yields of pollutants and byproducts were found:

1. Tar yield increased with rank from lignite to bituminous. This is inconsistent with data reported for the Lurgi and Wellman-Galusha gasifiers.

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2. Phenol, cresol, and xylenols (PCX) yield decreased with increasing rank, except for Montana Rosebud coal.
3. Benzene, toluene, and xylene (BTX) yield increased with increasing rank from lignite to bituminous.
4. Tar from lignite and subbituminous coals had a higher proportion of acids than tar from eastern coals.
5. Tar from bituminous coals had a higher proportion of bases than tar from lignite and subbituminous coals.
6. Tar from bituminous coals had a higher proportion of cyclohexane insolubles than tar from lignite and subbituminous coals.
7. The sulfur content of gasification tars was dependent on the sulfur content of the feed coals.
8. More sulfur was retained in solid residues from lignite and subbituminous coals than in residues from bituminous coals. This is consistent with combustion behavior.
9. Except for Montana subbituminous coal, gasification tars are more concentrated in nitrogen than the feed coals.
10. Nitrogen retention in gasification residue did not vary consistently with rank. The highest retentions occurred in the residue from Wyoming subbituminous and Illinois No.6 bituminous coals.
11. No tar and very low levels of BTX were produced in the gasification of anthracite coal. High retentions of sulfur and nitrogen in anthracite residue were consistent with low carbon conversion.

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7.0 TRACE ELEMENT DISPOSITION IN THE RTI GASIFIER: RELATIONSHIP TO PROCESS CONDITIONS

Many potentially toxic trace elements are found in coal in varying concentrations.[1] The disposition of these elements in the various process streams during coal gasification is of concern because of the large amounts of coal projected to be substituted for diminishing oil and natural gas supplies. Prediction of the behavior of trace elements during gasification would be very useful in identifying and avoiding potential problems arising from the release of toxic trace elements to the environment resulting from the disposal of wastes or the utilization of products from gasification. In addition, trace elements may have unexpected effects on catalysts used during gasification, on product gas upgrading, or on process equipment. Catalyst or process water recycling increases the chances of a buildup of trace elements to harmful levels if the trace elements of concern have a tendency to concentrate in these streams. Although substantial information is available on the behavior of trace elements during coal combustion, little data exist from which trace element pathways in gasification processes may be established. It is hoped that the data presented in this report will help to define potential areas of concern in the behavior of trace elements during coal gasification and will clarify the relationship between process conditions and trace element volatilization.

Trace and minor element analyses on feed coals and effluents from the RTI gasifier were done by atomic absorption spectroscopy (AA) and neutron activation analysis (NAA). AA was performed in-house, while NAA was done at North Carolina State University (NCSU) by the Nuclear Services Laboratory. Details on the analytical techniques employed, quality control, and selection of standards may be found elsewhere.[2,3,4]

In all, 28 elements were analyzed in the product and effluents from 27 different gasification tests using various U.S. coals. However, not every process stream from every test was analyzed for trace elements, and all 28 elements were not determined in all samples. This report concentrates on

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ten elements: antimony, arsenic, beryllium, cadmium, chromium, lead, manganese, mercury, nickel, and selenium. These elements were chosen for several reasons. They are potentially toxic, have been previously identified as elements of concern for coal gasification,[5] have been shown to be volatile during gasification,[6,7,8,9] and have been found at significantly high levels in RTI gasifier effluents or in effluents from other gasifiers. This report concentrates on the results of tests using four coals: Illinois No.6 bituminous, North Dakota Beulah/Zap lignite, Wyoming Smith/Roland, and Montana Rosebud/McKay.

As mentioned before, the behavior of trace elements during gasification is important for environmental reasons and because of their potential effects on catalysts used during gasification or in product gas cleaning and upgrading. Although some studies exist which report trace element volatilization during gasification and the partitioning of trace elements in gasifier effluent streams,[6,7,8,9] little or no work has been done to relate the degree of volatilization of specific trace elements to process variables except on a theoretical basis.

Two major factors help determine the behavior of an element during gasification processes: the chemical form of the element in the raw coal and the process conditions during gasification. The chemical form of trace elements in coal depends upon several factors including the biogeochemical conditions during deposition in the original coal swamp, as well as the geological and geochemical factors to which the coal is subjected after burial. For example, the trace element mineralogy of western coals, which are relatively young, laid down in freshwater and are presently in a semiarid environment is considerably different from the trace element mineralogy of Illinois basin coals, which are considerably older, laid down in a more marine environment, and are presently in a fairly humid environment.[10] Process conditions, such as temperature, pressure, and residence time are the other major factors influencing trace element behavior during gasification. For example, one can predict more complete volatilization of volatile elements with high temperature slagging processes, such as the Koppers-Totzek or Texaco process, than with moderate temperature processes like Lurgi or Wellman-Galusha.

In order to relate process conditions to the degree of volatilization of individual elements, a simple linear correlation coefficient (r) was calcu-

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lated to relate the volatility of each element to the process variable in question. This is a rather simplistic approach considering the complex interaction of process variables during gasification and the complex chemical environment in the gasifier as a result of these interactions, but it does serve to point out trends, and basic relationships between, trace element chemistry and process conditions. Due to the low concentrations of the species in question, trace element analyses cannot be considered to be of high accuracy. This problem, along with problems in sampling nonrepresentative materials which may be quite heterogeneous on the microscopic scale, preclude the use of trace element data in more sophisticated models relating volatility to process variables.

In order to identify the effects of different coal types, correlation checks were performed on tests using a single type of feed coal. This report will emphasize correlations derived from tests using Illinois No.6 bituminous coal because more tests were conducted using Illinois No.6 coals. Depending on the element, 7 to 9 tests using Illinois No.6 have trace element data. Correlations were also performed for tests using Wyoming subbituminous coal (3 to 5 tests with trace element data) and North Dakota lignite (4 tests with trace element data) for comparison with the Illinois No.6 correlations.

The fraction of each element volatilized during gasification was calculated using the equation:

$$\frac{C\ ash}{C\ coal} \cdot \frac{M\ ash}{M\ coal} \cdot 100 = \text{percent volatilization} \qquad (1)$$

where C ash and C coal are the concentrations (ppm) of the element in question in the gasifier residue and in the coal; and M ash and M coal are the total mass of the gasifier residue and of the coal. Linear correlation coefficients (r) are calculated for percent volatilization vs. individual process variables such as temperature, pressure, air/steam ratio, air/coal ratio, steam/coal ratio, carbon conversion, or sulfur conversion. A correlation is considered to be valid only if the level of confidence for the correlation coefficient (r) is equal to, or greater than, 90 percent.

Little correlation was found between reactor temperature or pressure and trace element volatility. This is not surprising considering that these parameters are held fairly constant from test to test. Pressure was maintained

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at 200 psi, except for 2 tests carried out at 30 psi. Only lead volatilization appears to have changed for these tests, with an especially low volatilization during low pressure tests. Temperature was also maintained at a fairly constant level, with maximum reactor temperature ranging from 911° to 1089°C. Greater variations in temperature would probably have a greater effect on trace element volatilization, with increasing temperature causing increased volatility.

The following is a discussion, by element, of trace element behavior in the RTI gasifier.

ARSENIC

The major repository for arsenic in the RTI gasifier was the residue. For 20 tests, arsenic recovery in the residue ranged from 20 to 100 percent of the arsenic input to the reactor, with a mean recovery of 76 percent. However, because of the toxicity of this element, the factors affecting its volatility during gasification are of concern.

For tests with Illinois No.6 coal, arsenic volatility was found to correlate strongly with carbon conversion ($r = 0.935$) and sulfur conversion ($r = 0.899$) (Figure 7-1). These correlations were calculated from nine samples (7 degrees of freedom) and therefore are significant at a level greater than 99.9 percent. Carbon conversion is essentially a measure of the extent of gasification; that is, the longer the residence time, the more complete the gasification of the carbonaceous material and the greater the fraction carbon converted to gaseous and liquid products. For moderate temperature low-Btu gasification processes like the RTI gasifier, using bituminous coals, a continuous release of the arsenic may be expected during gasification after a certain carbon conversion is reached with more complete volatility occurring as carbon conversion increases. Little or no volatilization of arsenic was detected for tests with carbon conversions at or below 87 percent. This implies that for the RTI gasification tests using Illinois No.6 coal, arsenic volatilizes during the latter stages of gasification.

The correlation between arsenic volatility and sulfur conversion is not surprising. Arsenopyrite (FeAsS) has long been identified as the most likely form of arsenic in eastern and Illinois basin coal.[11] Recent scanning electron microscopy on eastern coals has confirmed the presence of arsenic

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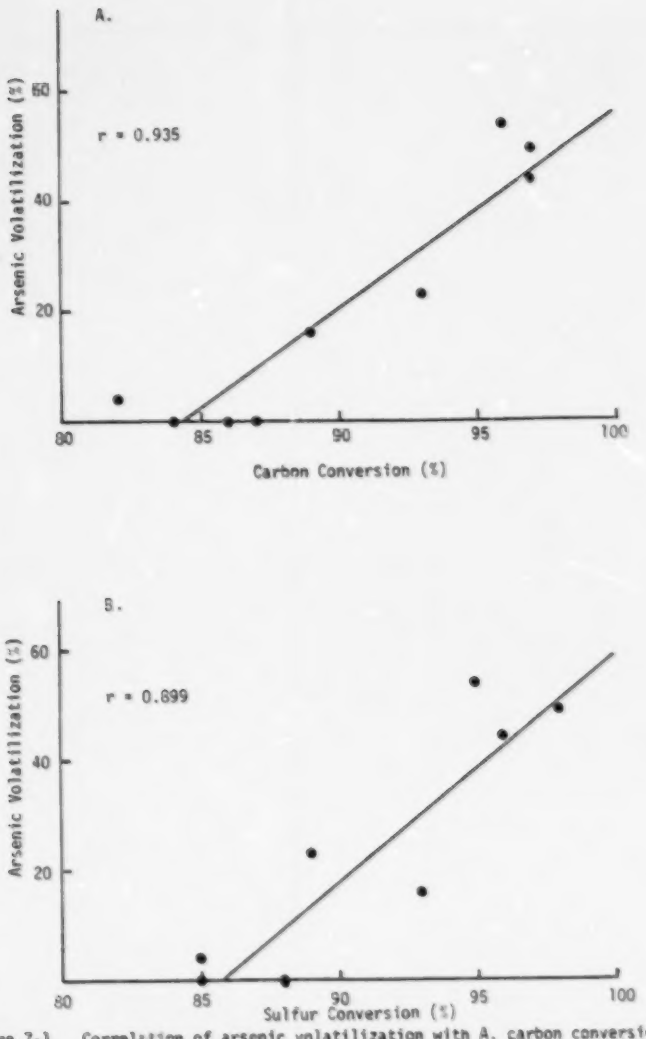

Figure 7-1. Correlation of arsenic volatilization with A. carbon conversion and B. sulfur conversion. Gasification tests with Illinois No.6 coal.

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as reaction rims on pyrite crystals.[12] Most of the sulfur in Illinois No.6 coal is present as pyrite. Therefore sulfur conversion is an indication of pyrite conversion. Since arsenic is associated with pyrite, it follows that arsenic volatilization correlates with sulfur conversion.

Arsenic volatility did not correlate with sulfur or carbon conversion for tests with North Dakota lignite or tests using the western subbituminous coals. This implies that arsenic is not found in the same form in these coals as in the Illinois No.6 coal. This is consistent with analyses which indicate that pyrite (and therefore the sulfide minerals associated with it) is generally found in lower concentrations in western coals than in the coals from the Illinois basin.[10]

For tests using North Dakota lignite, a negative correlation was found between arsenic volatility and air/coal (g/g input) ratio ($r = -0.931$, 93 percent confidence level). The decrease in arsenic volatility with increasing air/coal ratio could be due to fixation of arsenic in the residue through oxidation. However, these correlations are based on only four data sets (4 gasifier tests) and therefore could be coincidental. No significant correlations were found between process variables and arsenic volatility for the western subbituminous coals.

Arsenic analyses of aqueous condensates from 14 RTI gasification tests indicated that from 3 to 98 percent of arsenic volatilized during gasification reported to the aqueous effluent stream. Up to 45 percent of the arsenic originally present in the feed coal reported to the aqueous condensate. This is in agreement with trace element studies on other gasifiers which indicate that a significant portion of the arsenic input into the reactor ends up in the condensate liquor.[6,7,8,9] This is especially significant for high temperature gasification processes, such as Texaco or Koppers-Totzek, where more or less complete volatilization of arsenic occurs and for processes, such as the Texaco process, where aqueous liquor recycle could possibly lead to a buildup of arsenic levels in the liquor. Depending on the arsenic concentration in the feed coal, there is a potential for high concentrations of arsenic occurring in the aqueous effluent streams from these processes.

Arsenic also was detected in the tar from the RTI gasifier. From 0.2 to 8.3 percent of arsenic in the feed coal reported to tar. This arsenic may represent organometallic arsenic compounds in the tar. Assuming that

any arsenic not detected in the residue, water, or tar effluents was contained in the gas stream, from 0 to 29 percent of the arsenic in the feed coal left the gasifier in the product gas. This gaseous arsenic is possibly in the form of arsine (AsH_3), forming from arsenic vapor and hydrogen under the reducing conditions during gasification.

To summarize, the gasifier residue is the major repository of arsenic in the RTI gasifier. A significant amount of arsenic is volatilized during gasification, with most of it reporting to the aqueous condensate and possibly to the product gas. Arsenic volatilization during the gasification of Illinois No.6 coal correlates strongly with sulfur conversion and carbon conversion. Gasification tests with western coals and lignite do not show these correlations.

SELENIUM

Selenium showed greater volatility than arsenic, with from <0.9 to 44 percent of the element in the feed coal being recovered in the residue. The mean recovery of selenium in the residue was 26 percent for 13 tests. Selenium is therefore very volatile during gasification.

For tests with Illinois No.6 coals, selenium volatilization correlates with carbon conversion with a correlation coefficient (r) of 0.893; the correlation, based on 7 tests (5 degrees of freedom), represents a significance level lying between 99 percent and 99.9 percent (Figure 7-2). Unlike arsenic, significant selenium volatilization (60 percent) occurs even for tests with the lowest carbon conversion. Selenium is thus more volatile than arsenic in the RTI gasifier.

Selenium volatilization does not correlate with sulfur conversion for tests with Illinois No.6 coal. This suggests that selenium is not associated with sulfur in the Illinois No.6 coal. Float/sink studies on Illinois basin coals indicate that selenium is intermediate in behavior between organically associated elements and inorganically associated elements.[1] Our study implies that during gasification of Illinois No.6 coal, organically combined selenium is the volatile form. However, more complete data are needed to confirm these relationships.

Selenium correlated strongly with carbon conversion for gasification tests using Wyoming (Smith/Roland) and Montana (Rosebud) subbituminous coals

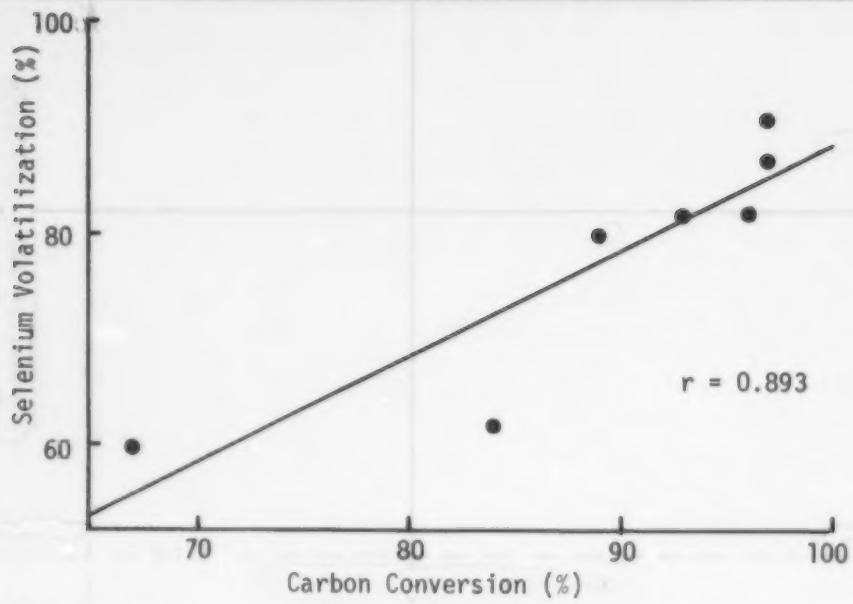

Figure 7-2. Correlation of selenium volatilization with carbon conversion during gasification of Illinois No.6 coal.

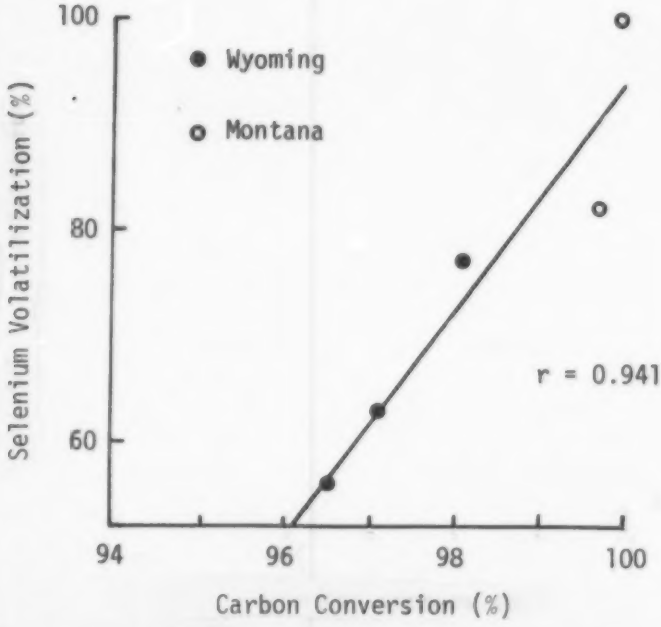

Figure 7-3. Correlation of selenium volatilization with carbon conversion during gasification of western subbituminous coals.

(Figure 7-3). Data from five tests were used in this correlation and the correlation coefficient (r) was 0.941, which gives a correlation significance level of about 98 percent. Limited analyses of condensate samples suggest that a significant fraction of the selenium input into the gasifier (from 12 to 38 percent) is present in the condensate water for tests with Illinois No.6 coals. Thus, along with arsenic, selenium could be of concern in the aqueous condensate liquors from the gasification of certain U.S. coals. Some selenium (from 1 to 8 percent of the amount in the feed coal) is present in the gasifier tar, but from 33 to 55 percent of the selenium input cannot be accounted for in the residue, water, or tar effluent streams. There is, therefore, a good possibility that significant amounts of selenium are leaving the gasifier in the product gas. Theoretical studies of selenium chemistry during gasification suggest that selenium present in raw product gas is almost entirely selenium hydride.[13] Further work involving product gas analysis is necessary to confirm this hypothesis.

ANTIMONY

Data on antimony disposition in the RTI gasifier are limited, but residue analyses for three tests with Illinois No.6 coal show a correlation ($r = 0.99$) with carbon conversion (95 percent significance) and a correlation ($r = 0.928$) with sulfur conversion (<80 percent significance). These correlations suggest a behavior similar to arsenic. Antimony thus may be in the form of a sulfide, although float/sink studies consistently place it in the organically associated group of elements.[1] Further study is needed to understand the behavior of antimony during gasification, although low concentrations of antimony in coal and coal residues make this a fairly low priority concern.

MERCURY

Mercury was very volatile during RTI gasification tests. Mercury was below the detection limit in the residue and condensate for all tests with untreated Illinois No.6, Wyoming Smith/Roland, Montana Rosebud coal, and North Dakota lignite. Small amounts of mercury were detected in tar samples from tests with Illinois No.6 coal, Wyoming Smith/Roland coal, and North Dakota lignite.

Mercury showed essentially complete volatilization in the RTI gasifier. None of the volatile mercury reported to the aqueous condensate, but a small amount, from 0.5 to 1.7 percent of that present in the feed coal, was detected in the tar. The presence of mercury in the gasifier tar was not surprising because mercury forms a myriad of organic compounds due to the ease with which mercury replaces hydrogen in organic compounds.[14] Many of these compounds are remarkably stable, being virtually unaffected by air or water.[14] Thus mercury in the tar is probably in organometallic compounds.

Except for the small amount in the tar, the bulk of mercury in the feed coal passed out of the gasifier in gaseous form. Although the gaseous mercury compounds in gasifier product gas have not been identified as yet, predictions on probable forms of mercury in product gas have been made based on thermodynamic considerations. These studies suggest that the thermodynamically preferred gaseous species leaving the gasifier is elemental mercury, Hg.[13] Based on this assumption from 8.55×10^{-10} to 1.03×10^{-7} g-mol, Hg/g-mol product gas would be expected, depending on the gasification process and the amount of mercury in the feed coal.[13] The highest predicted concentration was for Koppers-Totzek gasification of coal containing 1.6 ppm mercury. Some of this volatile mercury would be expected to condense out of the product gas as it cools.

Interestingly, the addition of alkali metal catalysts changed the volatilization behavior of mercury during gasification. Illinois No.6 coal treated with 20 percent potassium carbonate (K_2CO_3) was gasified in test 54, and Illinois No.6 with 2 percent sodium hydroxide was gasified in tests 56 and 58. The addition of the alkali metal catalysts appears to have decreased the volatility of mercury in tests 54 and 56. These tests showed retention in the residue of 8.4 percent (test 54) and 9.0 percent (test 56) of the mercury in the feed coal. Mercury is known to form amalgams with sodium and potassium which have significantly higher melting points than the individual elements.[14] It is possible that these amalgams are being formed in the residue of tests with added sodium or potassium catalysts. Test 58 is interesting in that no mercury was detected in the residue in spite of the addition of 2 percent NaOH to the feed coal. This is perhaps due to the different process conditions during this run. No air was introduced to the reactor during the first 20 minutes of test 58, in contrast to continuous

air flow to the reactor from coal drop on during other tests. The first 20 minutes of test 58 was therefore essentially a pyrolysis of coal in steam and nitrogen. The absence of air during the initial stages of gasification seems to have prevented the fixation of mercury in the residue. This implies that mercury is volatilized during the early stage of gasification, since this appears to be the critical time in the fixation of mercury in the residue by alkali metals.

Environmentally, the fixation of mercury in the residue by alkali metal catalysts is not of concern because the concentration of mercury is very low, from 5 to 10 ppb, well below the DMEG (health) value of 200 ppb. However, for processes like the Exxon Catalytic Gasification Process, which call for recycling the alkali catalyst, its amalgamation with mercury could possibly interfere with the recovery of the catalyst from the gasifier residue. Also, recycling the catalyst without removing the mercury amalgamated to it could conceivably lead to a progressive buildup of the concentration of mercury in the catalyst during each cycle. More research is needed to see if these potential problems are real.

LEAD

Lead volatilization in 8 RTI gasifier tests with Illinois No. 6 coal varied from 0 to 97 percent of the lead input to the reactor. Lead volatilization was found to correlate ($r = 0.897$, 99 to 99.9 percent significance level) with maximum reactor temperature (time averaged) for tests with Illinois No.6 coal. Two tests (50 and 54) show little (0.6 percent) or no lead volatilization. These tests are interesting in that they are the only two tests which were terminated prior to oxygen breakthrough (i.e., before O_2 was detected in the product gas). This implies that oxygen may have some role in the volatilization of lead during gasification. The test during which there was zero lead volatilization (test 50) was a low pressure (30 psig) test. This suggests that lead volatility may be affected by pressure, with increased volatility with increased pressure.

Lead volatilization did not correlate significantly with any process conditions for the tests with North Dakota lignite. However, lead volatilization did show a weak correlation with the sulfate sulfur in the residue ($r = 0.846$, ~85 percent confidence level) and a stronger negative correlation

with pyritic sulfur in the residue (r = 0.990, 99 percent confidence level) and the organic sulfur in the residue (r = 0.917, ~92 percent confidence level). No correlation was evident between sulfur conversion and lead volatilization. Since the proportion of sulfate sulfur in the residue compared to pyritic and organic sulfur is probably sensitive to the degree of oxidation the residue has experienced, this supports the hypothesis that oxygen plays a role in the volatilization of lead during gasification. In addition, lead volatilization was very low (0.55 percent of the input lead) in a low pressure test with North Dakota lignite. This, along with the low volatilization of lead during low pressure tests with Illinois No.6 coal supports the hypothesis that lead volatilization is increased by increasing pressure during gasification.

For 5 tests with Montana and Wyoming coals, lead volatilization again correlated with sulfate sulfur in the residue (r = 0.810, 96 percent confidence) (Figure 7-4). This is in further support of the hypothesis that oxidation increases lead volatilization. No other significant correlations were found for lead volatilization during tests with western coals.

Only small proportions of the input lead reported to the condensate (0.1 to 9.0 percent of the input lead) or to the tar (0.05 to 4.5 percent of the input lead). From 69 to 98 percent of the volatile lead (or 17 to 65 percent of the total input lead) was unaccounted for in all tests, and thus may be assumed to be exiting the reactor in the product gas. Since lead does not form especially volatile compounds such as hydrides, much of the lead in the product gas would be expected to condense out as the product gas cools.

In summary, lead volatilization was found to correlate with time-averaged maximum reactor temperature for RTI gasifier tests with Illinois No.6 coals. Oxidation and pressure seem to affect lead volatilization in all tests, with increases in residue oxidation or pressure increasing lead volatilization.

Lead analyses of gasifier effluents were conducted only for tests using Illinois basin or western coals. X-ray fluorescence analyses using a scanning electron microscope indicate that the dominant form of lead in western coals and in coals from the Illinois basin is galena.[15] These same studies indicate that the major form of lead in Appalachian coals is lead selenide (PbSe).[15]

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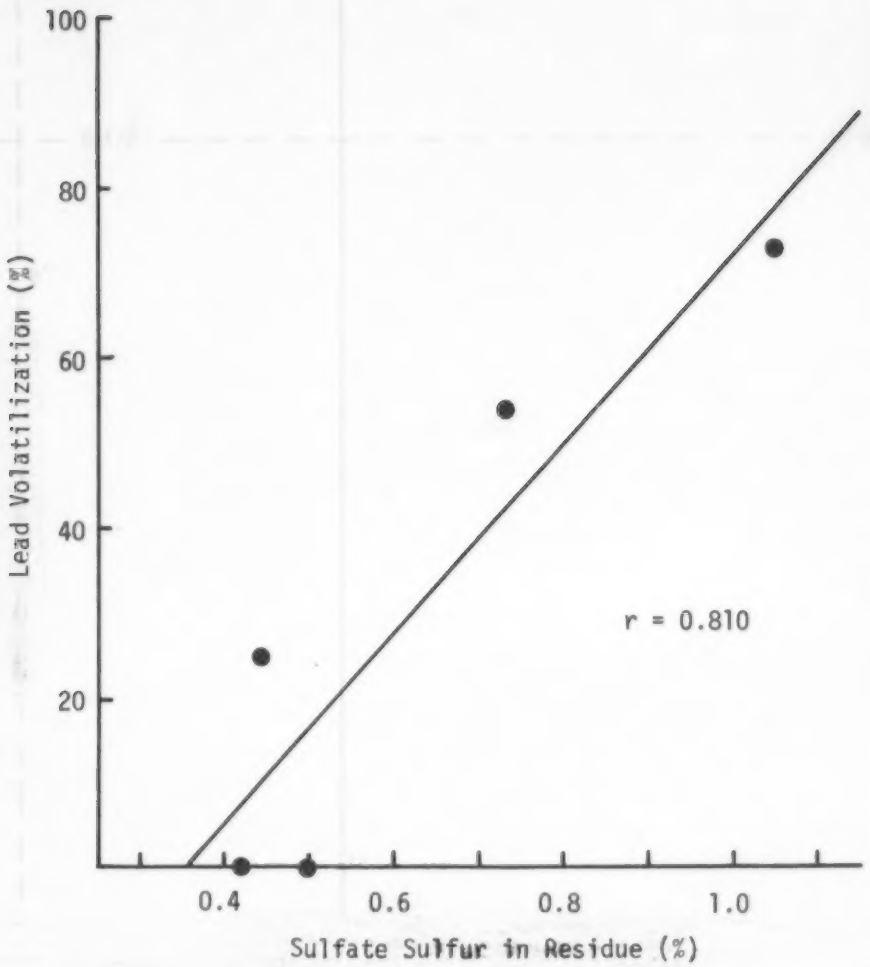

Figure 7-4. Correlation of lead volatilization with sulfate sulfur in the residue for gasification tests with western subbituminous coals.

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Thus lead may exhibit different behavior during the gasification of Appalachian coals compared to other U.S. coals.

BERYLLIUM

Based on float/sink studies, beryllium has a very high organic affinity in all U.S. coals.[1] That is, it is probably present in organic form. However, in tests with Illinois No.6 coal in the RTI gasifier, beryllium was strikingly nonvolatile. Only one out of five tests with untreated Illinois No.6 coal showed significant beryllium volatilization. During this test (23), beryllium that was volatilized was 18 percent of the total beryllium input to the reactor. No reason for this volatilization could be deduced by examining the process conditions during this test. Beryllium also showed no volatilization during a test using an 80 percent Illinois No.6, 20 percent K_2CO_3 catalyst mix (test 54). However, the two tests with 2 percent NaOH added to Illinois No.6 coal showed beryllium volatilizations of 21 percent (test 54) and 43 percent (test 56) of total beryllium input. The addition of sodium hydroxide thus appears to have interfered with the fixation of beryllium in the gasifier residue.

Tests with North Dakota lignite and with western subbituminous coals showed greater volatilization of beryllium. From 0 to 54 percent of the beryllium in the feed coal volatilized during the gasification of North Dakota lignite, from 33 to more than 92 percent of the input beryllium volatilized during the gasification of Wyoming Smith/Roland coal, and from 5 to 12 percent of the input beryllium volatilized during the gasification of Montana Rosebud coal. No significant correlations were found between beryllium volatilization and process variables for any of these tests.

No beryllium was detected in the aqueous condensate or tar from any of the tests. It appears that volatile beryllium leaves the reactor with the product gas.

CHROMIUM, NICKEL, AND MANGANESE

These elements were all found in excess amounts in the gasifier residue. A larger amount of these elements was present in the residue than was present in the feed coal for all tests. Excesses, expressed as percent of element input to the gasifier detected in the residue, ranged up to 23,000 percent for chromium, up to 63,000 percent for nickel, and up to 619 percent for

manganese. It can be safely assumed that these huge excesses are the result of the erosion of the stainless steel reactor walls under the high temperatures and reducing atmospheres of gasification. Similar excesses for these elements were reported in a trace element study of ash from the Lurgi gasifier in Westfield, Scotland. The excesses of these elements at Westfield are not nearly as great as those found in the RTI gasifier ash, but this may be because of the larger scale of the Lurgi gasifier which results in less steel surface area per unit volume of product gas and/or a difference in reactor alloy composition. The erosion of steel reactors is of concern because of the real potential for forming highly toxic carbonyl compounds of nickel or chromium in reducing atmospheres. These carbonyl compounds would represent definite occupational hazards to those working in close proximity to the gasifier. In addition, erosion of a steel reactor could lead to levels of these metals in effluent streams which are high enough to be of environmental concern. Chromium, manganese, and nickel enrichment is not expected to be a problem for gasifiers with refractory-lined reactors.

CADMIUM

Cadmium was found to be extremely nonvolatile during most tests with untreated Illinois No.6 coal. Only one test showed any cadmium volatility. Cadmium volatilization was 39 percent of the amount in the feed coal for test 46. It is not clear why cadmium volatilized during this test, although this test had the highest maximum temperature (1112°C) and the highest air input to coal input ratio (4.60) of all tests with Illinois No.6 coal.

Cadmium is more volatile during the gasification of North Dakota lignite and Wyoming subbituminous coal. From 13 to greater than 87 percent of the cadmium in the feed coal was volatilized during the gasification of North Dakota lignite. From 43 to greater than 98 percent of the input cadmium was volatilized during the gasification of Wyoming subbituminous coal. No significant correlations between cadmium volatilization and process variables could be found for these tests.

The following conclusions on trace element behavior during gasification can be made based on examination of the data from trace element analyses of RTI gasifier. Because the data are from a limited number of runs from a single gasifier, these conclusions are hypothetical in nature. More data from

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other gasifiers are necessary to definitely confirm or reject these hypotheses.

1. Arsenic volatilization during the gasification of Illinios No.6 coal correlates strongly with carbon conversion and sulfur conversion. The major repository for arsenic during gasification is the residue. Most of the volatile arsenic is present in the aqueous condensate and in the product gas.
2. Selenium volatilization is significantly correlated with carbon conversion but not with sulfur conversion for gasification tests using Illinois No.6 coals. A similar correlation was seen for tests with Wyoming subbituminous coal. Most of the volatile selenium is found in the product gas and in the aqueous condensate.
3. Mercury shows complete volatilization during gasification of all coals except for tests with added alkali catalysts. The addition of alkali metals fixes some mercury in the residue, possibly through amalgamation. Most of the volatile mercury is found in the product gas, with a little reporting to the tar.
4. Lead volatility appears to be increased by increasing pressure during gasification. Oxygen also seems to play some role in the volatilization of lead with an increase in volatile lead in tests where the residue appears to be more oxidized. Most of the lead probably leaves the reactor in the product gas, with condensation expected as the gas cools.
5. Beryllium and cadmium are nonvolatile during the gasification of Illinois No.6 coal. Both show greater volatility during the gasification of western coals, and the addition of NaOH increases the volatility of beryllium during the gasification of Illinois No.6 coal.
6. Large excesses of chromium, manganese, and nickel were detected in the residues and other effluents for all gasification tests. These excesses are probably due to the erosion of the stainless steel reactor. The formation of highly toxic compounds of nickel and chromium in these reactors is possible, and should be considered a potential occupational hazard during their operation.

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8.0 POLLUTANT EVOLUTION IN PYROLYSIS TESTS

During gasification runs in the RTI reactor, pollutants were evolved in two main stages. First, a surge period of rapid gas evolution occurred immediately after the coal was dropped into the reactor. A second period of lower gas evolution rates occurred after pyrolysis was complete when steam and air were admitted to the reactor. The gases produced during the second stage result from gasification and combustion reactions of the char which remains after pyrolysis.

The compounds of largest environmental concern--tars, sulfur compounds and phenolics--are predominantly formed in the pyrolysis, or surge period. Even hydrogen sulfide and carbonyl sulfide, the main pollutants which evolved during the gasification stage, are formed much faster during pyrolysis. Figure 8-1 shows compound evolution rates for North Dakota lignite as presented in an earlier RTI report dealing with several coals.[1] Note that the evolution rates for sulfur compounds and aromatic hydrocarbons drop by a factor of 10 to 100 after the initial surge period.

Since most of the reactions of interest occur during the first stage, tests involving pyrolysis only were made in the RTI reactor. The objective was to determine the effects of particle size, bed depth, and surrounding atmosphere in the absence of oxygen or steam feed. The product gases were sampled at short intervals until pyrolysis was completed. The runs were made at 200 psig using a Smith-Roland Wyoming subbituminous coal fed in a batch manner. The results and their interpretation follow.

EXPERIMENTAL PROGRAM

The experimental technique for the pyrolysis experiments was much like that followed in the semicontinuous gasification experiments discussed earlier. The reactor walls were preheated by using the surrounding three-zone furnace prior to the run. At the start of the run, the coal was dropped into the bed and an upflow of preheated sweep gas was begun. Samples

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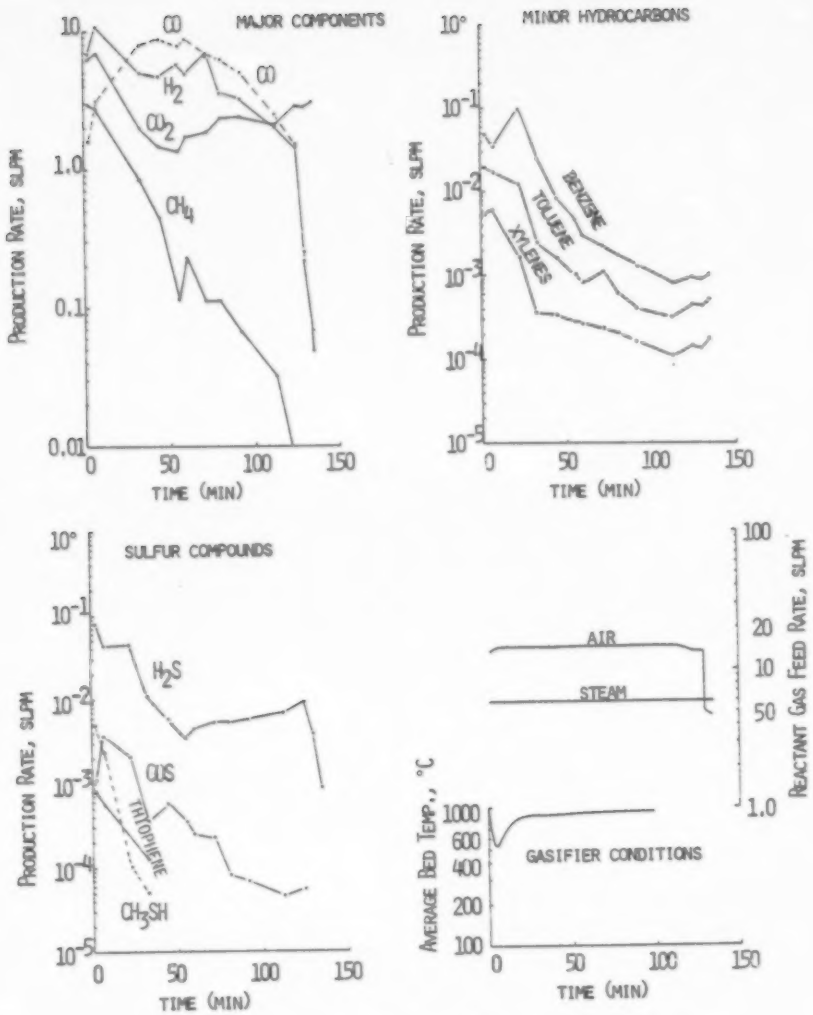

Figure 8-1. Gasifier results; run 36, North Dakota lignite.

of the product gas were taken in glass bulbs at short intervals downstream of the pressure controller and the tar/water condensers.

A series of six runs were conducted on Wyoming Smith-Roland subbituminous coal. A subbituminous coal was selected because lower rank coals are more likely candidates for the commercial gasifier which the RTI system most closely models--a dry-bottom, fixed-bed process. The characteristics of the coal used are shown in Table 8-1. A summary of the other test conditions is presented in Table 8-2.

The reactor pressure, the furnace wall temperatures, bed temperatures as measured by an internal thermocouple, inlet gas flow, and inlet gas temperature were the most pertinent variables for the pyrolysis tests. Figure 8-2 presents example results for the basecase run. Other runs showed similar values.[2] Times at which samples of the product gas were collected in glass bulbs are shown on the time axis.

EVOLUTION PROFILES FOR PYROLYSIS PRODUCTS

The pattern in which product gases were given off after the coal drop was similar for most of the gas species measured. Immediately after the coal was dropped into the hot reactor, the evolution rate of each gas species rose sharply to a maximum value. The evolution rate then quickly dropped to some intermediate value on a gently declining plateau before again plummeting to a very low value at the completion of pyrolysis. Figure 8-3 demonstrates the effect as seen for CO_2, CH_4, CO, and H_2 evolved during the basecase run. (The "peak-plateau" profile for evolution rates occurred entirely within the pyrolysis phase in the RTI reactor. The effect should not be confused with the two-stage division noted earlier between pyrolysis and gasification periods. The gasification reactions are independent of and occur after pyrolysis is complete.)

HEAT TRANSFER AND TEMPERATURE PROFILES IN THE RTI REACTOR

For pyrolysis runs, the empty reactor was preheated by external electric heaters while a preheated inlet gas was being fed through the bottom distributor plate. After obtaining steady temperature conditions, a coal charge at room temperature was dropped into the hot reactor in a very short time. The resulting effect is the same as if the bed of coal had already

TABLE 8-1. CHARACTERISTICS OF WYOMING SUBBITUMINOUS COAL USED IN PYROLYSIS RUNS

Sample	Proximate Analysis Wt % (as received)	Ultimate Analysis Wt % (dry basis)	Sulfur Forms Wt % (dry basis)
8 x 16 Mesh Particles	Moisture 25.56	Carbon 70.28	Pyritic Sulfur 0.10
	Volatile Matter . . 22.10	Hydrogen 4.72	Sulfate Sulfur 0.00
	Fixed Carbon 47.16	Nitrogen 1.09	Organic Sulfur 0.51
	Ash 5.18	Chlorine 0.01	
	Btu (as received) 8,733	Oxygen* 16.33	
	Btu (dry basis) 11,731	Ash 6.96	
	Free Swelling Index 1/2		
4 x 8 Mesh Particles	Moisture 24.11	Carbon 70.74	Pyritic Sulfur 0.06
	Volatile Matter . . 21.53	Hydrogen 4.73	Sulfate Sulfur 0.00
	Fixed Carbon 49.08	Nitrogen 1.17	Organic Sulfur 0.54
	Ash 5.28	Chlorine 0.15	
	Btu (as received) 9,000	Oxygen* 15.65	
	Btu (dry basis) 11,859	Ash 6.96	
	Free Swelling Index 1/2		

*By difference.

TABLE 8-2. SUMMARY OF PYROLYSIS TEST CONDITIONS

Test	Coal Charged (g)	Coal Size (U.S. Mesh)	Carrier Gas Flow (SLPM)	Carrier Gas	Comments
P1-Basecase	1500	8 x 16	60	100% N_2	No problems.
P2-Larger Particles	1500	4 x 8	60	100% N_2	Carrier gas flow varied ± 15% during run and was 4 minutes late being turned on. Otherwise all right.
P3-Lower Gas Flow	1500	8 x 16	20	100% N_2	Intermittent coal drop. Took 6 minutes to complete.
P4-Basecase Repetition	1500	8 x 16	60	100% N_2	Intermittent coal drop. Took 6 minutes to complete.
P5-Shallow Bed	500	8 x 16	60	100% N_2	Bottom furnace temperature was low. Otherwise all right.
P6-Reducing Atmosphere	1500	8 x 16	60	50% N_2; 25% H_2; 25% CO.	Bottom furnace temperature was low. Otherwise all right.

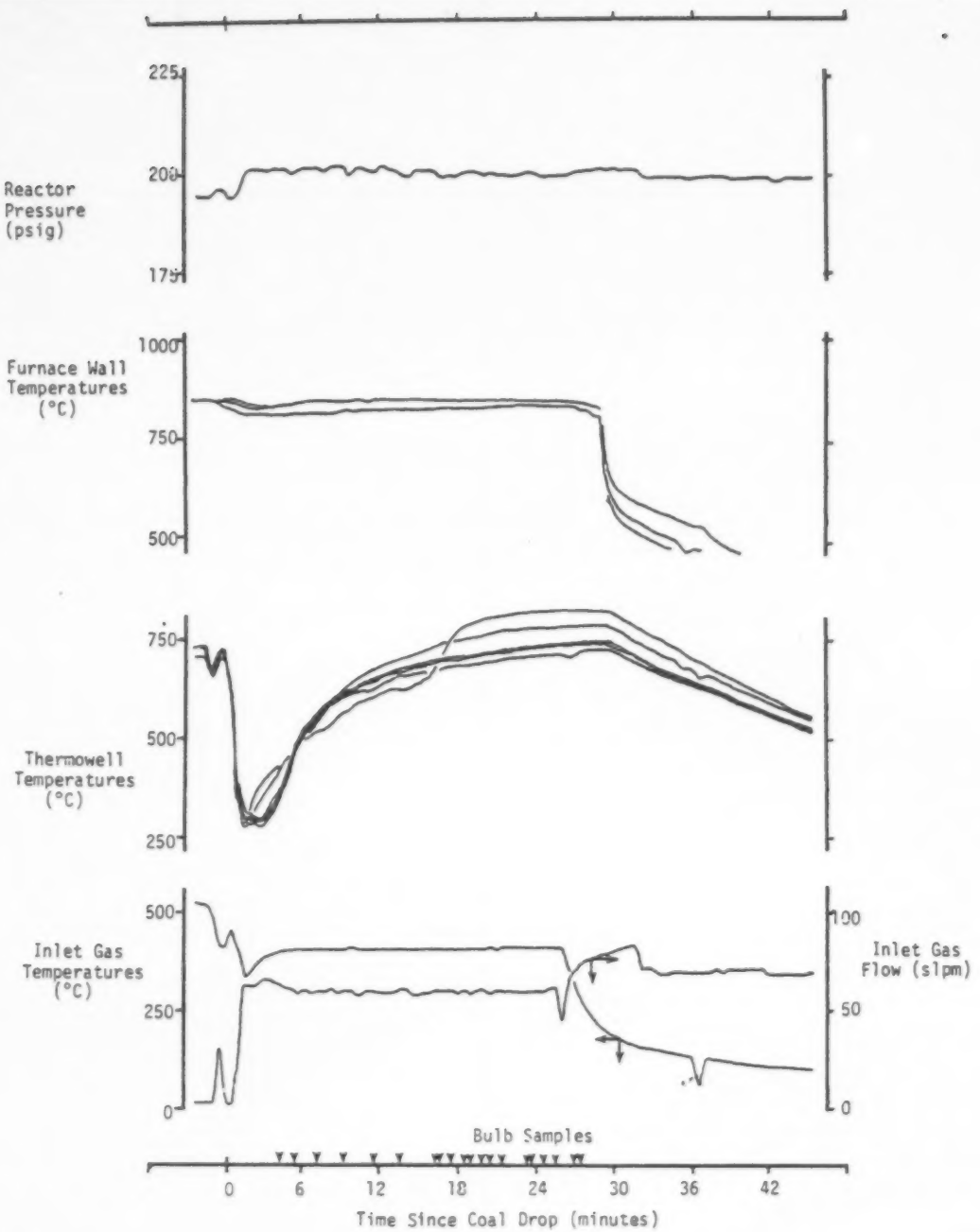

Figure 8-2. Operating conditions for pyrolysis test P-1: Base case.

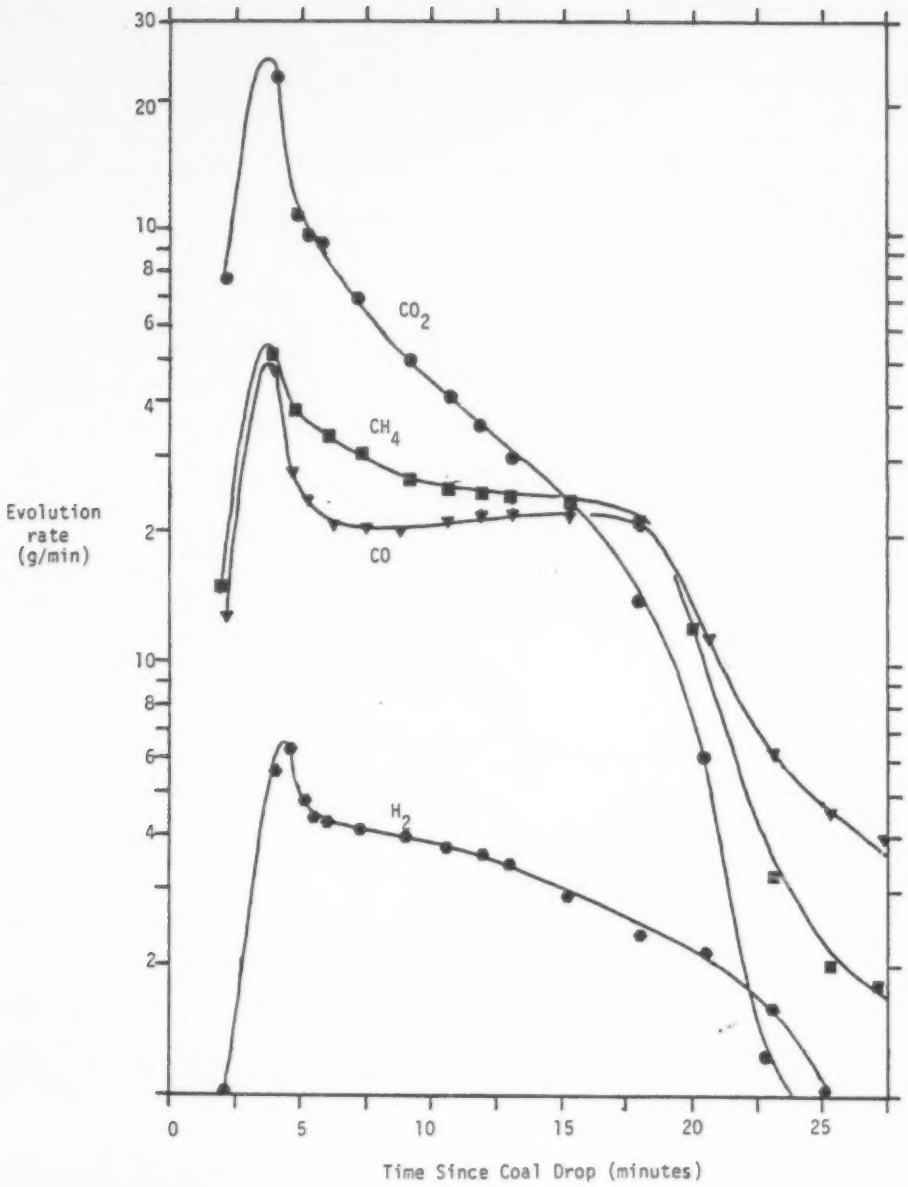

Figure 8-3. Evolution profiles for major gases from pyrolysis test P-1: Base case.

been sitting in a cool reactor when the wall temperature was instantly raised to some high value while hot gas was simultaneously admitted to the bottom of the reactor.

The temperature history which the coal undergoes in such a mode of operation is far from simple. The temperature of a single coal particle will vary with time since the coal drop, the distance from the bottom of the bed, and the distance from the center of the bed. Each location in the bed has associated with it some time-varying conditions of temperature, degree of conversion, etc.

A computer program was developed for evaluating particle temperatures in the RTI reactor. It computed the temperature profiles at any height or radial position in the bed. The program results compared well with the limiting cases of no gas flow and no heat conduction from the walls.

Roughly speaking, particles which are both in the lower one-third and inner one-half of the bed receive heat mainly from the incoming gas, not from the hot walls. Particle temperatures near the top of the bed are dominated by radial heat conduction inward from the walls, and the flowing gas has little effect. Intermediate locations are affected by both mechanisms of heat transfer. The complete model developed for the pyrolysis runs adequately represented the complex temperature profiles in these intermediate regions as well as reflecting the limiting cases.

KINETIC CALCULATIONS

The heat transfer model was developed so that it could be coupled with reaction kinetics to predict overall generation rates of individual compounds. In other words, by knowing how the reactor temperature changes at any location, the reaction rate versus time can be computed at each location and then combined to give the rate of reaction for the whole bed.

The bed was divided into 20 axial increments of equal length and 20 radial increments of equal area. Then temperature, rates, and fractional conversion were computed for each increment. The overall rate and conversion was then calculated by summing values for the individual increments. This series of calculations was repeated at each time step until conversion was complete. The reaction kinetics assumed irreversible, first-order dependence on unevolved material in the coal. The composition of the surrounding gas was assumed to have no effect on the pyrolysis reactions.

For kinetic parameters typical of pyrolysis reactions,[3] the model predicted the curves shown in Figure 8-4. Note the shape of the evolution profiles. An initial peak of high evolution rate is observed, followed by a more or less level rate period, and finally a rapid decay to zero rate at complete conversion. These are exactly the same profiles observed experimentally in the RTI pyrolysis runs. The unusual evolution patterns measured can thus be explained by the heat transfer patterns in the reactors as predicted by this model.

It was initially hoped that useful kinetic parameters might be obtained for individual pollutant generation. However, different combinations of activation energy and rate constant resulted in very similar evolution profiles. When experimental error and uncertainty in model parameters are considered, a wide range of kinetic parameters could fit the experimental data equally well.

Even though quantitative rate parameters could not be obtained, the kinetic model was extremely useful in interpreting the pyrolysis runs. Significant deviations from the predicted profiles pointed to important information on the mechanisms of pollution evolution.

POLLUTANT EVOLUTION

Figure 8-5 presents evolution rates for pollutant gases evolved during pyrolysis. Hydrogen sulfide, carbonyl sulfide, methanethiol, benzene, and toluene evolution rates are shown for the large particle run. In some of the other runs evolution rates for thiophene were also measured. These data came from gas chromatographic measurements taken of glass bulb samples of the dried product gas. They have been adjusted for changes in the gas flow, to yield mass evolution rate; since they cover large ranges, they have been plotted on semilogarithmic paper--g/min evolved versus time.

Data plotted in this manner are comparable to Figure 8-4 prepared from the kinetic model as described in the previous section. A conversion factor which adjusts for the total amount of each compound evolved is the only adjustment needed to directly compare the experimental data with Figure 8-4. Since the evolution rates are plotted on logarithmic scales, multiplying by such a conversion factor only shifts the entire curve up or

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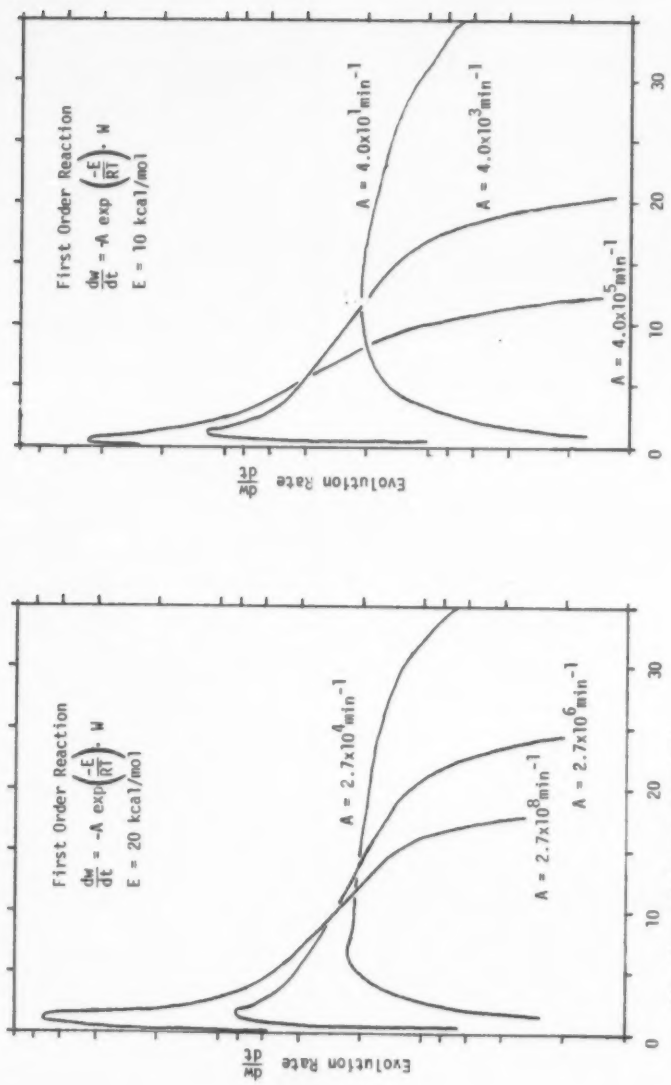

Figure 8-4. Evolution rates during pyrolysis as predicted by model of RTI reactor.

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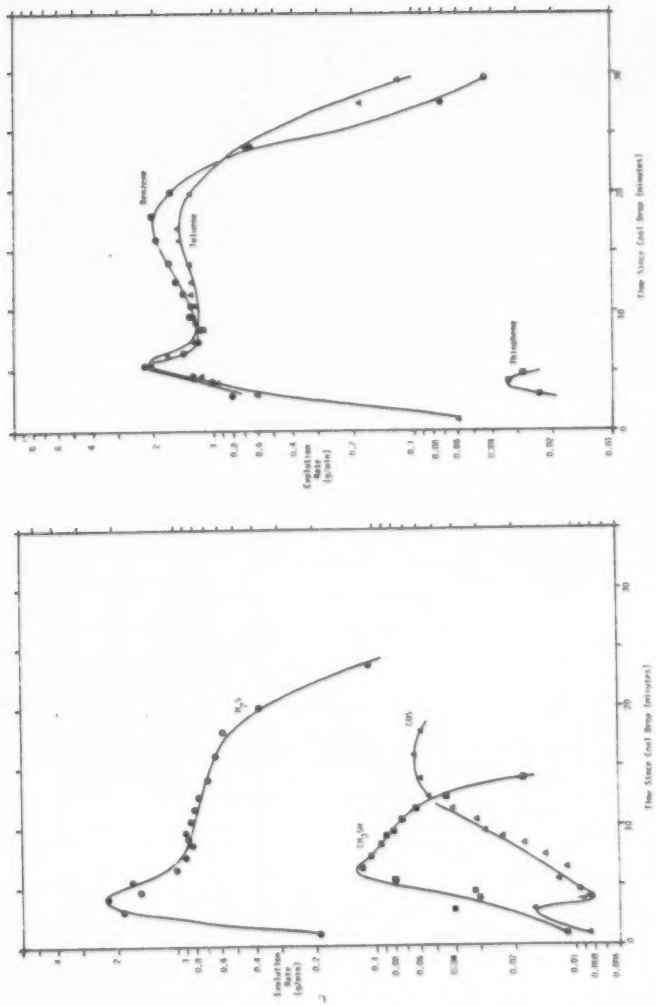

Figure 8-5. Evolution rates for pyrolysis test P-2: Large particles.

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down; it does not change the shape of the curve. Thus, compounds which have evolution curves whose shape markedly differs from those in Figure 8-4 must be compounds whose formation kinetics are poorly described by the model's assumptions (a first-order, irreversible reaction with no gas phase dependence).

Carbonyl sulfide, COS, was the only pollutant measured which showed an evolution pattern drastically different from that predicted by theory. For all other compounds which were measured, the maximum production rate occurred early in the run shortly after the coal drop. COS also showed a small increase early in the run, but the maximum production rate was measured much later when all the other compounds had already declined from their maximum evolution rates. This anomalous behavior is considered significant. It is believed that COS is mainly formed, not from breakdown of the coal structure during pyrolysis, but instead by later reactions between hydrogen sulfide and other gases present in the reactor.

The reaction proposed for COS formation are:

Reaction I: $H_2S + CO \rightleftarrows COS + H_2$

Reaction II: $H_2S + CO_2 \rightleftarrows COS + H_2O$.

The low rates of COS production early in the pyrolysis test might be attributable either to the inhibition of the reaction by water from the coal moisture, or to the fact that early in the run, most of the particle surfaces in the bed have not achieved temperatures high enough for the reaction to proceed. The second explanation is preferred, because calculations indicate that the COS level in the product gases is well below equilibrium levels for H_2S conversion to COS. The low level of COS thus implies that the rate of COS production is kinetically controlled.

Benzene and toluene were found to behave identically in all test runs. Not only did they evolve at the same time for each individual test, the same amount of each was produced for this coal. (It is not generally expected that all coals would produce the same level of benzene and toluene. The higher rank eastern coals would be more likely to have higher benzene production than toluene since they are more aromatic and contain fewer methyl side groups in the parent coal molecule). It seems reasonable that benzene

and toluene will be evolved during the same time period of pyrolysis regardless of coal structure, and that they are probably formed by the same mechanism.

Thiophene is an aromatic sulfur compound which has a ring structure much like benzene and toluene. One might expect that thiophene would evolve at the same time as benzene and toluene. For the runs in which thiophene production was measured, this was not at all the case. Thiophene is formed much sooner during the reactor heatup than either benzene or toluene. It is concluded that the mechanism of thiophene production is not the same as that of benzene/toluene production even though they are both aromatic ring compounds.

There was no significant difference in pollutant generation between the two sizes of coal particles studied: 8 x 16 U.S. mesh (2.3 to 1.19 millimeter) and 4 x 8 mesh (4.6 to 2.38 millimeter). The independence of pyrolysis rates on particle sizes in this range was confirmed in a separate set of experiments using thermogravimetric analysis (TGA). Particles of each size were subjected to heating rates typical of those in the RTI gasifier while having their weight continuously monitored by the TGA. The pyrolysis reactions as measured by total weight loss were the same for both sizes. It was interesting to note that in the TGA experiments pyrolysis did not depend upon particle size, but that moisture evolution from the coal by drying was significantly slower for the larger particles.

The sulfur compounds methanethiol (CH_3SH) and thiophene (C_4H_5S) evolved much earlier in the pyrolysis period than the other compounds which were measured: carbon monoxide, carbon dioxide, hydrogen, methane, benzene, toluene, and hydrogen sulfide. It is surprising that H_2S evolution more closely resembles the major gases (CO_2, CH_4, CO, and H_2) than it does the other sulfur-containing pollutants.

When pyrolysis occurred in a reducing atmosphere of nitrogen, hydrogen, and carbon monoxide, there was no effect on the level or the time of evolution for COS, thiophene, or methanethiol. However, the period over which benzene, toluene, and hydrogen sulfide were evolved was extended by the presence of the reducing atmosphere. It is speculated that the high level of hydrogen in the surrounding atmosphere enhanced the formation of H_2S and aromatic compounds which otherwise would have been limited by the amount of

aromatic compounds which otherwise would have been limited by the amount of hydrogen available from the parent coal structure. The unique behavior of carbonyl sulfide was not influenced by the presence of hydrogen and carbon monoxide. This further supports the postulate that COS formation is kinetically limited rather than equilibrium-controlled.

The high level of carbon monoxide would have increased the level of COS production if the production was equilibrium-controlled.

The following conclusions were drawn from the series of pyrolysis test runs.

1. Particle size and bed height had little influence on the rate or level of pollutant evolution from the RTI gasifier during pyrolysis.
2. The presence of an external reducing atmosphere during the pyrolysis period had little effect on the evolution profiles for thiophene, methanethiol, or carbonyl sulfide. The presence of hydrogen slightly extended the period of production for benzene, toluene, and hydrogen sulfide.
3. Of the pollutants studied, carbonyl sulfide displays unique behavior. Only a small amount is formed by the initial breakdown of the coal structure. Much more is formed later apparently via a kinetically controlled reaction with hydrogen sulfide.
4. Benzene and toluene evolve in an identical manner. For the Wyoming subbituminous coal investigated in these tests, not only was the period of evolution the same for both compounds, the level of production was also nearly identical.
5. Methanethiol and thiophene evolve very early in the pyrolysis reactions, while hydrogen sulfide (the major sulfur species) evolves over a longer time frame which is comparable to that of the major gases produced by pyrolysis--carbon dioxide, methane, carbon monoxide, and hydrogen.

References

1. McMichael, W. J., and D. G. Nichols, "Behavior of A Semibatch Coal Gasification Unit," In: Proceedings of Symposium on Environmental